

**MATHEMATICAL MODELING
OF TURBULENT REACTING PLUMES**

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*"Continued Development
of a Mathematical Modeling Capability
in Photochemical Air Pollution:
Reacting Plumes"*

Disclaimer

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**στους γονείς μου,
απο καρδιας**

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ABSTRACT

A new, comprehensive model for a chemically reacting plume, is presented, that accounts for the effects of incomplete turbulent macro- and micro- mixing on chemical reactions between plume and ambient constituents. This "Turbulent Reacting Plume Model" (TRPM) is modular in nature, allowing for the use of different levels of approximation of the phenomena involved. The core of the model consists of the evolution equations for reaction progress variables appropriate for evolving, spatially varying systems ("local phenomenal extent of reaction"). These equations estimate the interaction of mixing and chemical reaction and require input parameters characterizing internal plume behavior, such as relative dispersion and fine scale plume segregation. The model addresses deficiencies in previous reactive plume models. Calculations performed with the TRPM are compared with the experimental data of P.J.H. Builtjes (*) for the reaction between NO in a point source plume and ambient O₃, taking place in a wind tunnel simulating a neutral atmospheric boundary layer. The comparison shows the TRPM capable of quantitatively predicting the retardation imposed on the evolution of nonlinear plume chemistry by incomplete mixing.

Part IA of the present report (Chapters 1 to 3) contains a detailed description of the TRPM structure and comparisons of calculations with measurements, as well as a literature survey of reactive plume models. Part IB (Chapters 4 to 7) contains studies on the turbulent dispersion and reaction phenomena and plume dynamics, thus exposing in detail the underlying concepts and methods relevant to turbulent

* Builtjes, P.J.H. (1981) "Chemically Reacting Plume Experiments for the Wind Tunnel," Netherlands Organization for Applied Scientific Research, Division of Technology for Society, Ref. No. 81-013563, File No. 8710-20330.

reactive plume modeling. New formulations for describing in-plume phenomena, such as the "Localized Production of Fluctuations Model" for the calculation of the plume concentration variance are included here.

Part II is devoted to the presentation of the computer code implementation of the TRPM.

MATHEMATICAL MODELING OF TURBULENT REACTING PLUMES

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PART IA
MATHEMATICAL MODELING
OF TURBULENT REACTING PLUMES

General Theory,
Model Formulation and Evaluation

CHAPTER 1

PROBLEMS AND CONCEPTS OF REACTIVE PLUME MODELING

1.1 INTRODUCTION

All mathematical models of air quality offer an approximate description of actual meteorological-chemical systems that unavoidably relies on sets of simplifying assumptions. These assumptions are often based on specific information relevant to the phenomena to which they apply and thus their validity is supported by experience or theory (or both). However, in many cases simplifications are imposed on the mathematical formulation mainly by lack of adequate knowledge regarding the process considered. An example of the latter situation (often justified on an a priori requirement for simplicity) is the treatment of the effects of turbulent atmospheric mixing on the evolution of reactive systems by practically all large scale (urban or regional) models currently in routine use. The standard assumption involved in these models is that emissions are immediately mixed with the background air, in a perfectly uniform fashion, inside of some finite control volume (e.g. a computational cell of an Eulerian Grid model or an of "air parcel" following a Lagrangian trajectory). In this way the control volume is the analog of the ideal "stirred tank" of chemical reactor theory.

In fact pollutants emitted from strongly localized sources (industrial stacks) do not mix immediately with the background air at the molecular level but do so only

after a certain time has elapsed and a corresponding distance from the source has been travelled. This fact results in the existence of both mean concentration gradients and incomplete fine scale mixing that may be controlling factors in the spatial and temporal evolution of multimolecular reactive systems. Thus, for example, the actual rate of a bimolecular reaction (with relatively fast intrinsic kinetics) between an emitted species and a constituent of the background air will depend on:

(a) The *mean values* of the concentration of both reactants which vary from point to point not only in the direction of the wind but also in every cross-section of the plume, especially in the vicinity of the source. (Here mean values will always refer to ensemble averages unless explicitly stated otherwise). This is a state of incomplete "macromixing" in the relevant fluid-mechanical terminology. For a reaction with nonlinear kinetics, rates and conversions evaluated with concentrations of the two species averaged over the plume cross-section (or over any finite volume) will differ from the actual average rates and conversions over the cross-section (or the finite volume).

(b) The *state of mixing at the molecular level* ("micromixing"). Even if the mean concentrations of the two species are steady and non-zero at a point, instantaneous fluctuations about these mean values, due to the fact that molecular diffusion has not yet mixed the reactants uniformly at the molecular level, will retard the reaction rate. (*)

The above facts are often ignored and in most existing reactive plume models (as well as in practically all large scale air pollution models, as it was mentioned earlier) it is typically assumed that plume constituents and background air are assumed uniformly mixed - i.e. there are flat concentration profiles and no concentration fluctuations - over some finite area or volume. This assumption is equivalent to

(*) Reactions between species that coexist in the source emissions will also be influenced by concentration gradients and local fluctuations, although in that case delayed dilution of the reactive material with the background air will lead to higher actual rates than those predicted for a situation of complete mixing (as long as the reaction is of order higher than unity). Only monomolecular systems will be completely insensitive to these effects.

spatial averaging. Another type of averaging is implicitly introduced through the use of dispersion schemes that are relevant to *absolute* diffusion, and therefore to time-averaged concentration fields. However, when nonlinear reactions occur, temporal averages of reactant concentrations at a point do *not* give, when introduced into the dynamic equations that contain the nonlinearities, the corresponding averages of rates, conversions and product concentrations. This simple fact, which is often ignored in atmospheric modeling, dictates the use of statistics of instantaneous and not time-averaged realizations of the plume in the treatment of nonlinear reaction rates. Thus it is necessary to adopt transport closure schemes that account for the *non-local* character of turbulent dispersion and are able to discriminate between processes that affect the time averaged but not the instantaneous properties of the plume.

Various approaches, usually focusing on some particular aspect of the mixing-reaction problem, have appeared in the literature relevant to turbulent reactive plume (and in general turbulent reactive flow) modeling. However, these approaches have been either overly simplistic, thus corresponding to unrealistic descriptions of the processes involved, or, at the other extreme, overly complicated for routine use. In view of this situation the present work aims to develop a model that, while being fundamentally sound by accounting properly for the effects of macromixing, micromixing and implicit averaging on nonlinear plume chemistry, at the same time is computationally simple and easy to apply. (*)

The analysis that follows examines mainly the interaction of mixing and chemistry in the case of localized releases in ambient turbulence. Many of the concepts that are introduced and the equations that are formulated here are quite general,

(*) In the general perspective of photochemical air pollution modeling, this work studies the importance of phenomena that are of "subgrid scale" from the viewpoint of urban scale airshed models, as well as the overall effect of atmospheric turbulence on chemical reactions (which, as will be shown, is especially important for localized sources) aiming to improve on the predictive methods that are currently applied. In particular, special attention will be given to a reactive system that is most sensitive to these phenomena because of its very fast reaction rate, while at the same time is among the most important that determine the evolution of complex photochemical air pollution processes, that is the ozone-nitrogen oxides photolytic cycle (see Section 1.3 and Chapter 3).

holding for arbitrary ambient flows and a wide range of source conditions. However, the applicability of the current operational version of the model (as summarized in Chapter 2) is necessarily limited to situations for which the flow dynamics are sufficiently simple so as to allow a reduction of the overall phenomenon to processes involving parameters that can be reliably estimated. More specifically, in the present work the focus is on a plume advected by a mean wind field that is either uniform over a significant period, or, in general, changes "smoothly enough" in space and time so that a mean plume centerline can be defined. Then atmospheric motions that do not contribute to the mean field (random fluctuations) are responsible for the spread of the instantaneous plume and for its meandering about the mean centerline (depending on the magnitude of the spatial scale of these motions relative to the local plume "diameter"). Bulk meandering motions are also assumed sufficiently "mild", following Gifford's (1959) classic "fluctuating plume model".

1.2 POINT SOURCES IN CONNECTION TO LARGE SCALE AIRSHED MODELING AND THE ATMOSPHERIC DIFFUSION EQUATION

The structure, capabilities and limitations of large (urban) scale models as well as various problems related to their formulation and application are discussed extensively elsewhere (see, e.g., Turner, 1979; Benarie, 1980; McRae et al, 1982) and, being beyond the scope of this work, will not concern us here except to identify briefly the points for which the present work attempts an improved treatment.

As it was stressed in the introduction of this chapter (Section 1.1), inherent in all urban and regional air quality models are procedures of temporal and spatial averaging of both the velocity and the concentration fields at scales that vary with the particular model formulation. Thus, *single-box* models assume that the total mass of pollutants emitted from both localized and distributed sources in the area covered by the box is immediately mixed uniformly into the atmospheric air mass of the box. *Lagrangian Trajectory* and *Eulerian Grid models* allow for more resolution of the atmospheric field under consideration; however again uniform mixing down to the molecular level is assumed to hold at all times inside the computational cells independently of the localized character of some sources. (*) Although the description can be improved in principle by reducing the size of cells near localized sources the assumption of immediate uniform mixing over a finite volume remains. The size of the cells employed in grid models depends not only on limitations set by the numerical procedure but also on the character of available inputs and the formulation of the basic model equations (Seinfeld, 1975).

(*) In some cases (see, e.g., McRae et al., 1982; Stewart and Liu, 1981) improvements have been introduced in the grid models by combining them with simple "plume calculations" that at least account for reduced mixing volume near the source. In these formulations the plume is assumed to expand gradually to the size of a computational cell. The qualitative principle of this coupling between airshed and plume models is shown schematically in Figure 1-1.

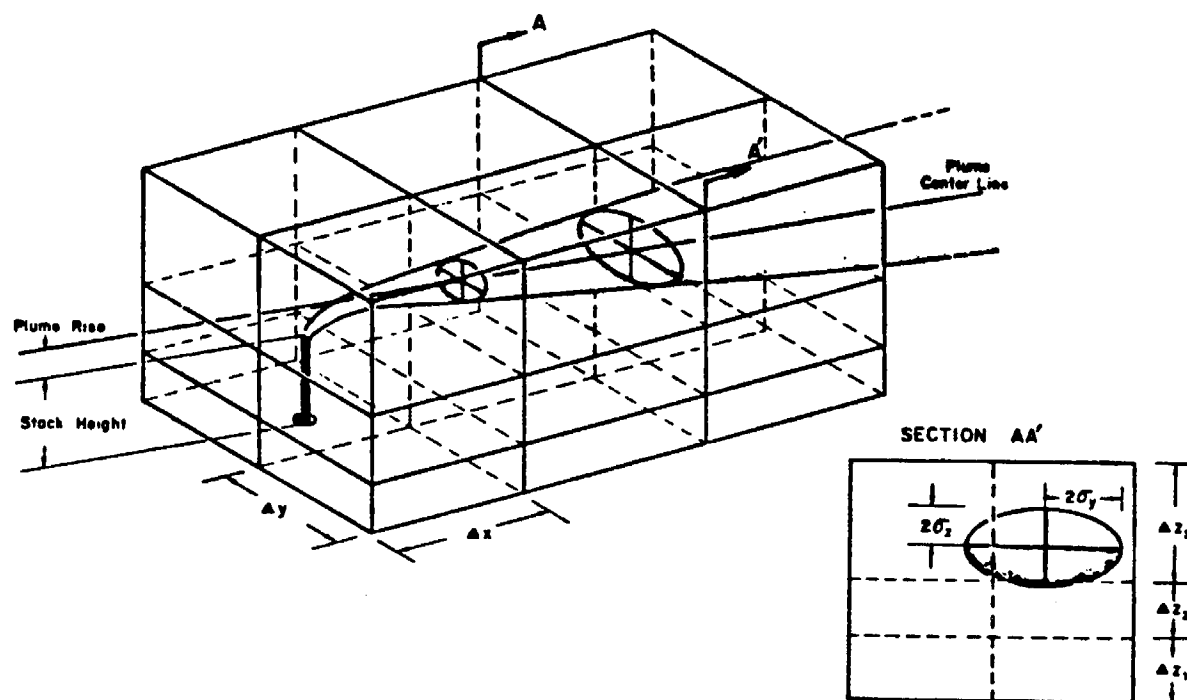


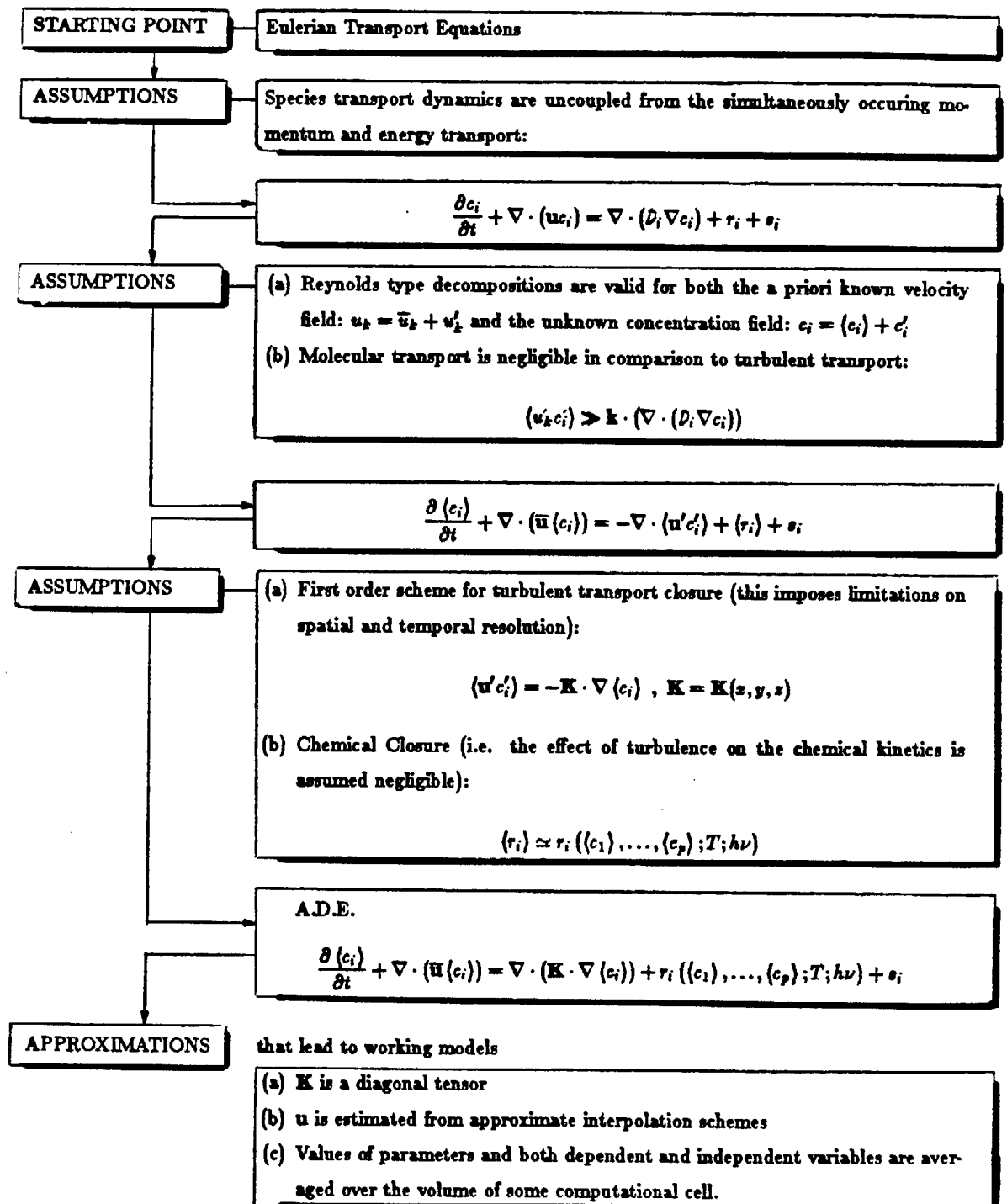
Figure 1-1
A Point-Source Plume Expanding
in the Grid of an Airshed Model.

For example, models based on the atmospheric diffusion equation (ADE) introduce *implicitly* minimum resolution space-time scales, through the first order closure scheme (K-theory) for turbulent transport which formulates the ADE (see Figure 1-2 and Table 1-1) starting from an ensemble averaged form of the stochastic species transport equation (which is assumed to hold instantaneously and pointwise in the atmospheric continuum). Nevertheless, since higher order closure schemes are drastically constrained from routine applicability because of their high computational burden and limited range of verified parameters, the K-theories employed in the common ADE still offer the most practical description of atmospheric processes currently in use in urban scale airshed models. Conforming to the requirement for a "reasonable" computational effort the present work will also rely on special first order transport closure schemes that extend the validity of the ADE to localized emissions and fast nonlinear chemistry, subject of course to different restrictions in applicability. (*)

These closure schemes are based on the alternative view of local phenomena that is offered by the well known Gaussian plume formulas, commonly available for non-reacting species. These can be interpreted as solutions of ADE-type equations but with eddy diffusivities that depend on the distance from the point source (Csanady, 1973; Pasquill, 1974) and therefore do not represent properties of the turbulent flow field but of the particular plume (i.e. of the particular dispersion process).

The picture of the dispersion given by the Gaussian plume equation depends on the nature of the parameters that are used; it is usually a time averaged picture (the "plume envelope") corresponding to parameters that describe absolute diffusion. Nevertheless the Gaussian equations formally also apply to the *ensemble mean* of the instantaneous realizations of the plume with the direct introduction of parameters that describe the process of relative diffusion. This fact extends the applicability of

(*) The conditions for the validity of the common ADE are discussed extensively in other works (e.g. Lamb, 1973; Corrsin, 1974; Seinfeld, 1975, 1983; Goodin et al., 1976; McRae et al., 1982 etc.); a brief summary of its limitations – that can also be seen as "sources of error" in applications where these limitations are typically ignored – is presented in Table 1-1.



(See Seinfeld, 1975; McRae et al., 1982 for notation and details)

Figure 1-2

Derivation of the Atmospheric Diffusion Equation

Table 1-1
Primary Sources of Error in the ADE
and in Related Air Quality Models

SOURCE OF ERROR	COMMENTS
A. The true form of the turbulent fluxes is unknown; a first order scheme (K-theory) is introduced to describe them.	<i>Higher order closure schemes offer improved description over eddy diffusivities. However such closure methods lead to large computational requirements.</i>
B. The closure approximation for turbulent transport limits the temporal and spatial resolution of the ADE. Inherent averaging leads to errors:	<i>Higher order closure schemes may allow formulation of equations with increased resolution capabilities. For point sources there is a simple first order closure alternative in the use of Gaussian plume models, corresponding to solutions of ADE-type equations, with eddy diffusivities that are functions of the travel time from the source. Proper selection of such diffusivities is needed for the description of instantaneous realizations of point source plumes.</i>
B.1. in the case of strongly localized sources which cause steep gradients of the mean concentration fields	
B.2. when combined with fast nonlinear chemical reaction rate terms.	
C. Fine scale turbulent fluctuations of the concentration fields that induce higher order correlations in nonlinear chemical kinetic terms are neglected.	<i>Models of turbulent kinetic rates that account for the effects of fluctuations may be introduced when such effects are found to be important.</i>

the Gaussian plume concept (and of the related governing equations) to problems involving nonlinear phenomena. Meandering, which determines the random instantaneous position of the plume, will have to be considered a posteriori when temporal or spatial averages of dependent variables of the nonlinear phenomena are to be estimated from their (expected) instantaneous point values.

Conventional K theories (with eddy diffusivities independent of the travel time) describe only time averaged pictures of the dispersion phenomena and thus cannot discriminate the two different effects comprising dispersion for the separate treatment that is needed when nonlinear phenomena occur. A solution to the problem of describing the transport dynamics of an expected instantaneous realization of a reactive plume is to use generalized "eddy diffusivities" defined in terms of the relative dispersion parameters of a Gaussian plume. Thus the resulting "modified" ADE will describe a particular dispersion process determined by the initial and boundary conditions (or source terms) relevant to a specific localized source, and will not be a "concentration transport equation" in the traditional Eulerian sense. Essentially it will be an implicitly "non-local" equation, a fact that forbids superposition of forcing terms. The formal justification of this description (which is often a subject of discussion and – sometimes unsupported – criticism in the literature) and the underlying implications relevant to the nature of the processes involved are analyzed in more detail in Chapter 6.

Before closing this brief discussion we must stress the fact that the special problems associated with nonlinearities of plume phenomena are relevant only if the rates of time evolution of these phenomena are comparable to those of the processes of dispersion. This point is elaborated in the next section (and in more detail in Chapter 4) in connection with nonlinear rates of chemical reactions.

1.3 TURBULENT KINETICS AND THE ATMOSPHERIC DIFFUSION EQUATION

In typical application of the ADE in air quality models two critical assumptions are made with respect to chemical reaction terms. The first is an implicit one, regarding the approximation of ensemble means by spatial and temporal averages and is imposed by the nature of the common first order transport closure scheme, and can be circumvented by using the modified ADE, as discussed in the previous section. The second assumption is an explicit one, stating that (ensemble) mean reaction rates are functions of (ensemble) mean concentrations only and thus the latter replace directly instantaneous concentrations in the functional forms of the phenomenological kinetic laws:

$$\langle R(c_1, c_2, \dots, c_n) \rangle = R(\langle c_1 \rangle, \langle c_2 \rangle, \dots, \langle c_n \rangle)$$

Such an approach neglects altogether the effect of turbulence on nonlinear kinetic terms and the consequent need for chemical closure; it is actually the simplest and most drastic closure approximation. However the conditions for the validity of this approach are very restrictive (Lamb, 1973) requiring reaction time scales that are large compared to the time scales associated with the dispersion processes.

To provide perspective on this point, let us consider the problem of the release of species *A* in a turbulent background containing the species *B*. *A* and *B* react according to



and the instantaneous-pointwise rate of (1.3-1) is expressed in terms of the instantaneous-pointwise concentrations as

$$R = k_f c_A c_B - k_b c_P \quad (1.3 - 2)$$

Under conditions for which transport can be assumed practically decoupled from the simultaneous momentum and energy transfer that govern the velocity and tempera-

ture fields (Seinfeld, 1975 – Section 6.1), the instantaneous concentrations of A , B and P at any point will obey the species mass balance equations

$$\mathcal{L}^M c_S = r_S \quad (1.3 - 3)$$

(where S stands for A , B or P) with the appropriate boundary and initial conditions that also account for source terms. Here \mathcal{L}^M represents the overall *Eulerian Mixing Operator* (a linear *stochastic* operator) which has the form (with the summation convention employed)

$$\mathcal{L}^M = \frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} - D_S \frac{\partial^2}{\partial x_i \partial x_i} \quad (1.3 - 4)$$

where u_i are the components of the random instantaneous velocity field and D_S is the molecular diffusivity of species S . r_S is the formation rate of species S . Obviously

$$r_A = r_B = -R, \quad r_P = R \quad (1.3 - 5)$$

Boundary and initial conditions are assumed deterministic in this formulation; thus all randomness is due to the turbulent velocity field.

In an Eulerian framework one starts typically by introducing Reynolds type decomposition of the random variables in mean and fluctuating components, that is $\mathbf{u} = \langle \mathbf{u} \rangle + \mathbf{u}'$, $c = \langle c \rangle + c'$ in the equations, where $\langle \cdot \rangle$ stands for ensemble averages. This leads to a moments closure problem, unavoidable in turbulence theory. (Eulerian formulations for evolution equations of the entire pdf have analogous closure problems). Nonlinear reaction rates produce *self-interaction* effects causing the appearance of new unknown correlations in the chemical part of (1.3-3) (“turbulent kinetic terms”) in addition to the turbulent transfer correlations in the fluid-mechanical part. Thus

$$\langle \mathcal{L}^M c_A \rangle = -k_f (\langle c_A \rangle \langle c_B \rangle + \langle c'_A c'_B \rangle) + k_b \langle c_P \rangle \quad (1.3 - 6)$$

with

$$\langle \mathcal{L}^M c_A \rangle = \frac{\partial \langle c_A \rangle}{\partial t} + \langle u_i \rangle \frac{\partial \langle c_A \rangle}{\partial x_i} + \frac{\partial}{\partial x_i} \langle u'_i c'_A \rangle - D_A \frac{\partial^2 \langle c_A \rangle}{\partial x_i \partial x_i} \quad (1.3 - 7)$$

where incompressibility of the flow is assumed. Similar relations hold for the concentrations of B and P .

Now, unless

$$|\langle c_A \rangle \langle c_B \rangle| \gg |\langle c'_A c'_B \rangle|$$

is valid, calculations have to account for the effects of $\sigma_{AB} = \langle c'_A c'_B \rangle$ on the evolution of the system. An extensive literature has developed in relation to models that account for these effects either explicitly by deriving closure expressions for σ_{AB} , or, more commonly, by treating the phenomenon of incomplete mixing through various indirect approaches. Chapter 4 is devoted to the study of such modeling procedures, focusing on models appropriate to treat plume chemistry of either infinite or finite rate.

For the purpose of this introductory section it is sufficient to delineate the conditions under which $\langle c'_A c'_B \rangle$ is expected to be significant. If, for simplicity, it is assumed that $D_A = D_B$ and the linear reverse reaction is neglected one has the following equation for σ_{AB} :

$$\begin{aligned}
 & \frac{\partial}{\partial t} \langle c'_A c'_B \rangle + \overbrace{\langle u_i \rangle \frac{\partial}{\partial x_i} \langle c'_A c'_B \rangle}^{(I)} = \\
 & = \overbrace{\langle u'_i c'_A \rangle \frac{\partial \langle c_A \rangle}{\partial x_i} + \langle u'_i c'_B \rangle \frac{\partial \langle c_B \rangle}{\partial x_i}}^{(II)} - \overbrace{\frac{\partial}{\partial x_i} \langle u'_i c'_A c'_B \rangle}^{(III)} \\
 & + \overbrace{D \frac{\partial^2 \langle c'_A c'_B \rangle}{\partial x_i \partial x_i}}^{(IV)} - \overbrace{2D \left\langle \left(\frac{\partial c'_A}{\partial x_i} \right) \left(\frac{\partial c'_B}{\partial x_i} \right) \right\rangle}^{(V)} \\
 & - \overbrace{k_f \left[\langle c'_A c'_B \rangle (\langle c_A \rangle + \langle c_B \rangle) + \langle c'_A c'^2_B \rangle + \langle c'^2_A c'_B \rangle + \langle c'^2_B \rangle \langle c_A \rangle + \langle c'^2_A \rangle \langle c_B \rangle \right]}^{(VI)}
 \end{aligned} \tag{1.3-8}$$

As expected, new unknowns (third order correlations) appear in this equation as a consequence of the closure problem. However one can obtain a qualitative understand-

ing of the processes that influence the evolution of σ_{AB} by examining the significance of the various terms in (1.3-8). These terms represent

- (I) : convection of σ_{AB} by the mean velocity field.
- (II) : generation of σ_{AB} by mean gradients in c_A and c_B .
- (III) : transport of σ_{AB} by turbulent velocity fluctuations (that is turbulent diffusion of σ_{AB}).
- (IV) : transport of σ_{AB} by molecular diffusion.
- (V) : dissipation of σ_{AB} by molecular diffusion.
- (VI) : production or decay of σ_{AB} due to chemical reaction.

In the absence of mean gradients the behavior of σ_{AB} is governed by the processes of fine scale mixing (term V) and chemical reaction (term VI); then the ratio of these terms can be used as an a priori measure of the intensity of interaction between mixing and reaction. We express the dissipation in terms of an appropriate Corrsin length scale ℓ_d (Corrsin, 1952), which is a scale of magnitude intermediate to the micro- and macro- scales of the flow, analogous to the Taylor scale for velocity fluctuations, as

$$2D \left\langle \left(\frac{\partial c'_A}{\partial x_i} \right) \left(\frac{\partial c'_B}{\partial x_i} \right) \right\rangle \simeq \frac{mD \langle c'_A c'_B \rangle}{\ell_d^2}$$

where m is an integer commonly set equal to 2 (Donaldson and Hilst, 1972). In cases where the magnitudes of fluctuations can be assumed smaller than those of the mean values, term (VI) is approximated by $k_f \langle c'_A c'_B \rangle (\langle c_A \rangle + \langle c_B \rangle)$; then one can use

$$N_R = \text{Da}_{II} = \frac{k_f [\langle c_A \rangle + \langle c_B \rangle] \ell_d^2}{2D} \quad (1.3-9)$$

as a measure of chemistry—dispersion interaction. N_R is the ratio of characteristic time scales for mixing and reaction (a Damköhler dimensionless group); it allows the classification of 2nd order chemical reactions in *homogeneous* turbulent concentration fields (and with relatively low fluctuation levels) into slow, moderate and fast. When $N_R \gg 1$ (“instantaneous” or “very fast chemistry”), the characteristic time for chemical reaction is short compared to that for mixing, and the phenomenon is governed not by the kinetics but by the rate at which the reactants are brought together

at the molecular level by dispersive processes. When $N_R \ll 1$ ("slow chemistry"), concentration fluctuations are dissipated before they can affect the kinetics; in this situation the mean reaction rate is satisfactorily predicted by $k_f \langle c_A \rangle \langle c_B \rangle$ (see also Lamb, 1973). In other words, if the dissipative scale of turbulence is small and the reaction rate is very slow, then molecular diffusion can be expected to keep A and B well mixed (at the molecular level) and the correlation term $\langle c'_A c'_B \rangle$ is negligible. For intermediate values of N_R a complex coupling between transport and chemistry requires elaborate schemes of modeling. (In the literature this regime is often referred to as "moderately fast" or "intermediate rate chemistry").

Representative values of N_R for some atmospheric reactions are given in Table 1-2. Typical values of $D = 0.17 \text{ cm}^2/\text{sec}$ and $\ell_d = 5$ and 20 cm were used in (1.3-9) for these estimates. One notices the wide range of N_R values relevant to atmospheric reactions as well as the sensitivity to the magnitude of the dissipation scale. It must be further stressed that in actual field situations, and in particular in plumes, even when segregation is small enough for (1.3-9) to provide a useful means for judging the coupling of transport and chemistry, ℓ_d as well as mean concentrations will vary significantly from point to point with subsequent large variations in the local value of N_R . Thus, the same reaction could be characterized as slow, moderate, or fast in different stages of plume evolution. Conditions such that *locally* $N_R = O(1)$ are possible for most of the reactions of Table 1-2; nevertheless it is obvious that certain reaction systems (such as the ozone - nitrogen oxides system) are most sensitive to fine scale concentration fluctuations.

Table 1-2
 Typical Damköhler Numbers N_R
 for a Smog Chamber Experiment^(a)

REACTION	RATE CONSTANT (ppm ⁻¹ min ⁻¹)	CONCENTRATION (ppm)		N_R ^(b)	
		c_A	c_B	$l_d = 5\text{cm}$	$l_d = 20\text{cm}$
NO + O ₃ →	23.9	0.045	0.069	3.33	53.4
NO ₂ + O →	1.34 × 10 ⁴	0.253	1.94 × 10 ⁻⁸	4146	66474
NO ₂ + O ₃ →	0.05	0.253	0.069	0.018	0.32
NO + HO ₂ →	1.20 × 10 ⁴	0.045	1.56 × 10 ⁻⁶	662	10588
OLE + O ₃ →	0.15	0.005	0.069	0.014	0.22
O ₃ + HO ₂ →	1.5	0.069	1.56 × 10 ⁻⁶	0.13	2.03

(a) Smog Chamber Experiment SUR-119J at 180 min (Pitts et al., 1976)

(b) Damköhler Number:

$$N_R = \frac{\text{Dispersion time scale}}{\text{Reaction time scale}} = \frac{k(c_A + c_B) l_d^2}{2D}$$

$$(\mathcal{D} = 10.2\text{cm}^2\text{min}^{-1})$$

A final point that must be mentioned here is that in complex reaction networks (typical in photochemical air pollution) the importance of turbulent rates must be assessed in connection to "global" kinetic mechanisms involving the reacting species and not in connection to a single reaction step. Indeed, when a dispersion limited reaction is a member of a complex coupled system it may be so much faster than the other reactions that lowering its actual rate to the effective mixing rate will not change significantly the results of the overall kinetics.

1.4 REQUIREMENTS AND LIMITATIONS IN REACTIVE PLUME MODELING

As a conclusion of the discussion presented in the preceding sections it can be stated that the complexity of the various interacting phenomena taking place during the simultaneous mixing and reaction of point-source plumes in the atmosphere, and which must be taken into account in order that a model of the problem is realistic, will depend on:

(I) *The order of the chemical reactions under consideration.*

Monomolecular reactions (intrinsic linear kinetic rates) are insensitive to the state of mixing and are not affected by fine scale fluctuations. The existence of gradients of the mean concentration field in a plume cross-section results in locally varying rates and conversions but, since averaging procedures can be interchanged with other linear operators, the temporal and spatial averages of these quantities (rates, etc.) are the same independently of the way they were estimated. Of course prediction of local concentrations in the vicinity of the source requires a model other than the common ADE because of its inherent inability of the latter to handle highly localized sources. Bimolecular (as well as higher order reactions) are affected by the state of mixing. Thus, if the reaction occurs faster than the plume mixes uniformly with the background air the actual rate will be controlled by dispersion effects. A priori averaging of the governing equations does not give the same average concentrations of products as a posteriori averaging of instantaneous pointwise concentrations of the same species. Hence instantaneous realizations of the plume must be considered in any computational scheme instead of time averaged plume envelopes.

(II) *The relative rates of reaction and dispersion processes.*

When the reaction is sufficiently slow the combined action of turbulent and molecular diffusion dissipates both mean concentration gradients and local fluctuations before appreciable conversion of reactants to products takes place. In such a case assump-

tions of well mixed cells are sufficient and the standard treatments of air pollution models are valid. When, however, the reaction rate is comparable or faster than that of the dispersion processes, a complex coupling of mixing and reaction phenomena occurs and schemes evaluating the results of this coupling must be introduced.

(III) *The initial state of the reactants.*

The interaction of mixing and chemistry is essentially different for the cases of initially premixed reactants (both constituents of the source effluent stream) and of initially non-premixed reactants (reaction between a constituent of the plume and the background air). Thus, for premixed reactants and reactions of order higher than one, turbulence creates positively correlated fluctuations and increases the overall rate as the reaction proceeds faster at the high concentration spots, whereas the action of molecular diffusion finally depresses the overall rate. For non-premixed reactants, and reactions of order higher than unity, turbulent fine scale fluctuations depress the reaction rate. Molecular diffusion is necessary to bring the reactants in contact and for fast reactions it may actually control the overall rate.

Thus when the (nonlinear) kinetic rate of a plume reaction is fast or comparable to that of the dispersion processes a reactive plume model must:

- (i) be based on the instantaneous and not the time averaged realizations of the plume. These realizations must be modeled by uncoupling the effects of meandering (which does not interact with chemistry) from that of relative diffusion.
- (ii) not ignore the existence of mean concentration gradients in any instantaneous plume cross-section (which are in fact much steeper than those present in the time averaged plume envelope).
- (iii) estimate spatial and temporal averages of dependent variables in an a posteriori fashion from the instantaneous description of the reactive system (which means that after rates and conversions have been estimated for the instantaneous realization of the plume - which is in steady state - they must be "spread out" to the plume envelope volume in a proper probabilistic manner).
- (iv) include a scheme that estimates the effect of fine scale fluctuations on the chemical

rate.

- (v) include a scheme that estimates plume rise because of buoyancy and the distance from the source at which a final rise is obtained.

Further improvements on this formulation can be made by incorporating, if possible, schemes that evaluate buoyancy and wind shear effects on the dispersion of the plume, examining the effects of initial (thermal) source conditions on chemistry, etc.

The above requirements constitute a set of guidelines for the construction (and validation) of a Reactive Plume Model arising from the complexity of the physical phenomena and the need for their proper description.

A second set of requirements (or rather limitations) arises from the need that the model is sufficiently simple in order to be useful. Thus, a practically applicable Reactive Plume Model must:

- (i) be simple and versatile,
- (ii) require commonly available air quality, meteorological and source data as input parameters,
- (iii) be compatible, if possible, with existing components of airshed models.

Therefore, a final working model, constructed on the lines specified by these two groups of requirements, must represent in some way a balance between

- (A) *complexity that arises from an adequately realistic description of the physical processes, and*
- (B) *simplicity and versatility, so that the model is useful for practical applications.*

Now, before proceeding to show how the scheme developed in the present work attempts to conform to these requirements – which is done in Chapters 2 and 3, with a detailed analysis regarding the modeling schemes and the parameters used following in Chapters 4 to 7– we present a brief summary of the current status of research in Reactive Plume Modeling.

1.5. REACTIVE PLUME MODELS : A LITERATURE SURVEY

Most atmospheric plume models in general fall in one of the following three major categories:

- (i) Formulations dealing with the fluid-mechanical aspects of the problem in the near source region where the source buoyancy and "internal" plume turbulence are significant. These are the "plume rise models" resulting in a variety of schemes, from semi-empirical algebraic equations to complex numerical formulations (see Chapter 7).
- (ii) Schemes, ranging from fitting of empirical data to large numerical experiments in either Eulerian or Lagrangian frameworks, that aim in the improvement of the parameterization of inert dispersion from point sources, for a variety of scales and averaging times (see Chapter 6), and,
- (iii) Schemes that focus on the evolution of, most often linear – but sometimes complex, single phase or even multi-phase – reaction networks involving species emitted from point sources as well as constituents of the ambient atmosphere (Reactive Plume Models). The time scales relevant to this evolution correspond, almost exclusively, to the final or "atmospheric diffusion" phase of plume dispersion (i.e. typically beyond downwind distances of the order of magnitude of 100 stack diameters). Other physical removal processes (surface deposition, washout) may be included in these schemes.

At this point it must be mentioned that the resolution provided by some of the formulations commonly referred to as plume models is just that of urban (and even regional) models. Thus, certain of the currently available "plume" models, that consider complex nonlinear chemistry, are straightforward Lagrangian Trajectory models employing K-theory (despite the limitations discussed earlier) to describe turbulent transport inside the advected large Lagrangian volume; others employ Gaussian plume dispersion parameters but ignore the interaction of time averaging and nonlinearities. Appendix A1.2 contains a representative list of plume models, intended for

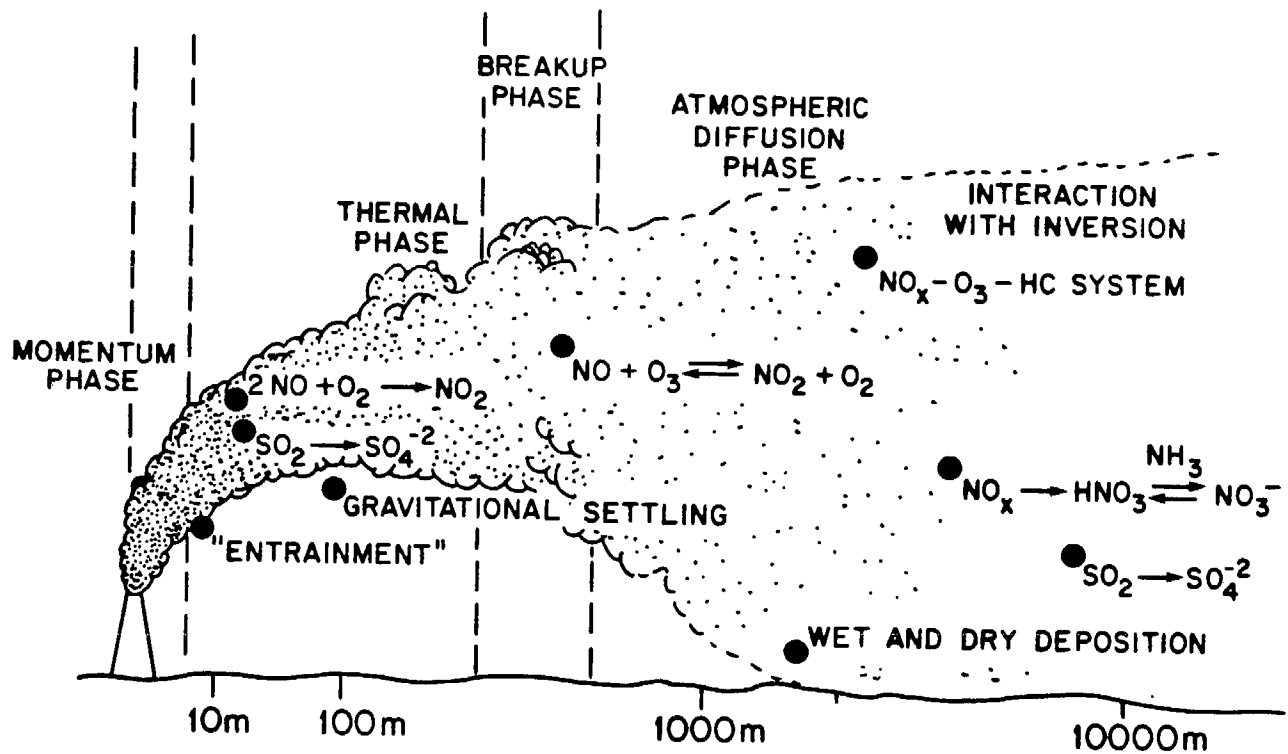


Figure 1-3

Schematic Representation of the Evolution
of the Various Typical "Phases" of Plume Physics and Chemistry
(and of the spatial scales associated with these phases).

routine use, that covers the typical range of available formulations; a brief description of each model is also presented there. More extended, comparative reviews of plume models and relevant references can be found in Liu et al. (1982) (see also Benarie, 1980).

Another point that cannot be overemphasized is the proper identification of the spatial/temporal range to which a particular model is relevant. To provide perspective on the importance of the different physical and chemical processes over various scales of the downwind distance from the source we give in Figure 1-3 a schematic representation of a "typical" plume evolving through successive "phases" where its initial momentum, its buoyancy, and, finally, the ambient turbulence, determine internal plume dynamics, rise, and expansion. (For further discussion of plume evolution and dominant processes in a given spatial range see Chapter 7 and Csanady, 1973).

Let us now focus attention on models that consider in-plume chemistry (in general more realistic than simple removal linearly related to the concentration level). Such models can be classified according to a variety of different criteria. A general review that examines different plume chemistry schemes and reactive plume models can be found in Burton et al. (1983); in the same volume (de Wispelaere, 1983) one can find summarized information on various aspects of particular in-plume processes. Typically, models incorporating large, complex, chemistry networks tend to simplify greatly the effects of the mixing processes. The most realistic and sophisticated representations of mixing are incorporated in formulations dealing with relatively limited reaction networks involving few reactions, most commonly with the $\text{NO-NO}_2\text{-O}_3$ photochemical system for which experience has shown the effects of mixing to be most important. Indeed, the fast reaction rates associated with this system and the fact that emissions from large industrial sources are in general rich in NO (and poor in hydrocarbons) make these reactions dominate plume chemistry in the earlier phases of dispersion where the volume of the plume gases is much smaller than that of typically sized cells of Eulerian grid (and most Lagrangian trajectory) models.

A review and classification of representative reactive plume models according to

the way they treat mixing processes follows. (*) This classification is also summarized in Table 1-3 and, schematically, in Figure 1-4, where typical concentration patterns, as treated by the various models, are presented. (For some further discussion of the in-plume concentration patterns – resulting from the interaction of chemistry and mixing – see Chapter 3, and in particular Figure 3-2 and the comments relevant to it.)

Class I

Models that account only for reduced initial dispersion volume occupied by point source emissions (smaller than the resolution scale of the ADE or the computational grid of an urban scale model). Mixing is assumed uniform in this reduced volume (flat mean profiles - no fine scale fluctuations). Examples are: Liu et al. (1975), McRae et al. (1982), Forney and Giz (1981), Cocks and Fletcher (1979), Varey et al. (1978), Isaksen et al. (1978).

Some of these models have been used in combination with urban scale airshed models, with the point source plume expanding gradually until it reaches the size of a computational cell. The expanding plume cross-section has been assumed either circular (Forney and Giz, 1981), rectangular (Liu et al., 1975) or elliptical (McRae et al., 1982). McRae et al. (1982) noted that the dispersion parameters determining the size of the elliptical cross-section must describe the instantaneous plume profile from relative dispersion and not the time averaged plume envelope. From the perspective of the present work it is very interesting to see how these simple models treat plume chemistry during the expansion of the plume; for this reason the formulation of McRae et al. (1982) is summarized in Appendix A1.1.

(*) This classification focuses on reactions with relatively fast nonlinear kinetics. As we have already noted slow reactions are adequately treated by conventional schemes that are currently in use (see McRae et al., 1982). Linear processes are naturally tractable (insensitive to the degree of micromixing) and analytical results are often available (e.g., Heines and Peters, 1973; Peterson and Seinfeld, 1977; Astarita et al., 1979; Alam and Seinfeld, 1981). However one should always keep in mind that the limitations on the validity of the ADE, regarding averaging and allowable temporal and spatial resolutions, are implicit in the results that are deduced from it, even when only linear processes are involved.

Table 1-3
Classification of Reactive Plume Models

DESCRIPTION OF MIXING	SELECTED REFERENCES
I. <i>Reduced initial dispersion volume</i> (<i>uniform mixing at any cross-section</i> <i>of this volume</i>)	Liu et al. (1975), Isaksen et al. (1978), Varey et al. (1978), Cocks and Fletcher (1979), Forney and Giz (1981), McRae et al. (1982)
II. <i>Divided perfectly mixed/unmixed</i> <i>dispersion volume</i>	Carmichael et al. (1981)
III. <i>Reduced Initial dispersion volume</i> <i>and</i>	
IIIA. <i>Sectionally homogeneous field</i> <i>at any cross section</i>	Lusis (1976), Melo et al. (1978), Stewart and Liu (1981), Hov et al. (1981), Seigneur et al. (1983)
IIIB. <i>Gaussian mean field</i> <i>at any cross section</i>	Peters and Richards (1977), White (1977), Hegg et al. (1977)
IV. <i>Turbulent fluctuations</i> (<i>no mean gradients</i>)	Donaldson and Hilst, (1972), Lamb (1976), Shu (1976), Shu et al. (1978), Bilger (1978), Kewley (1980)
V. <i>Mean field gradients</i> <i>and fine scale fluctuations</i>	Borghi (1974), Donaldson and Varma (1976), Kewley (1978)
VI. <i>Probability density evolution</i> <i>formulations</i>	Dopazo (1976), O'Brien et al. (1976), O'Brien (1980)

Class II

The partially perfectly mixed expanding volume: Carmichael and Peters (1981).

In the formulation of this model it is assumed that at every (circular) cross-section of the expanding plume only a fraction of the source effluent is perfectly mixed (flat profile—no fluctuations) with the environment. The rest remains pure source effluent forming a core surrounded by the perfectly mixed material. This core shrinks with distance from the source. The mixing process is viewed as a pseudo-kinetic step governed by empirical laws involving a mixing rate constant and the concentration of unmixed reactants. The advantage of such a model over those of Class I is only relative; completely empirical constants describing mixed and unmixed volume fractions must be introduced, and thus any improvement of predictions compared with those of the previous models is essentially a success in data fitting for the estimation of the constants.

Class III

Models that account for both reduced initial dispersion volume and inhomogeneous mean concentration fields (but consider no fine scale fluctuations) by:

Class IIIA:

assuming sectionally homogeneous fields or by

Class IIIB:

assuming Gaussian concentration fields inside the plume boundaries.

Thus, in models of Class IIIA the expanding plume volume is divided either in many expanding boxes of rectangular cross-section (Stewart and Liu, 1981; Seigneur et al., 1983; Hov et al., 1981), or in concentric elliptical rings (Lusis, 1976; Melo et al., 1978). In each of these sub-volumes the species are assumed perfectly mixed (flat profiles, no concentration fluctuations). The model of Stewart and Liu (1981) which is used in combination with an urban scale airshed model visualizes a cross-section of plume as an array of well mixed cells perpendicular to the plume centerline that expand in a prescribed fashion. The concentric elliptical rings model (Lusis, 1976; Melo et al., 1978) was developed for the NO-NO₂-O₃ system based on a similar model

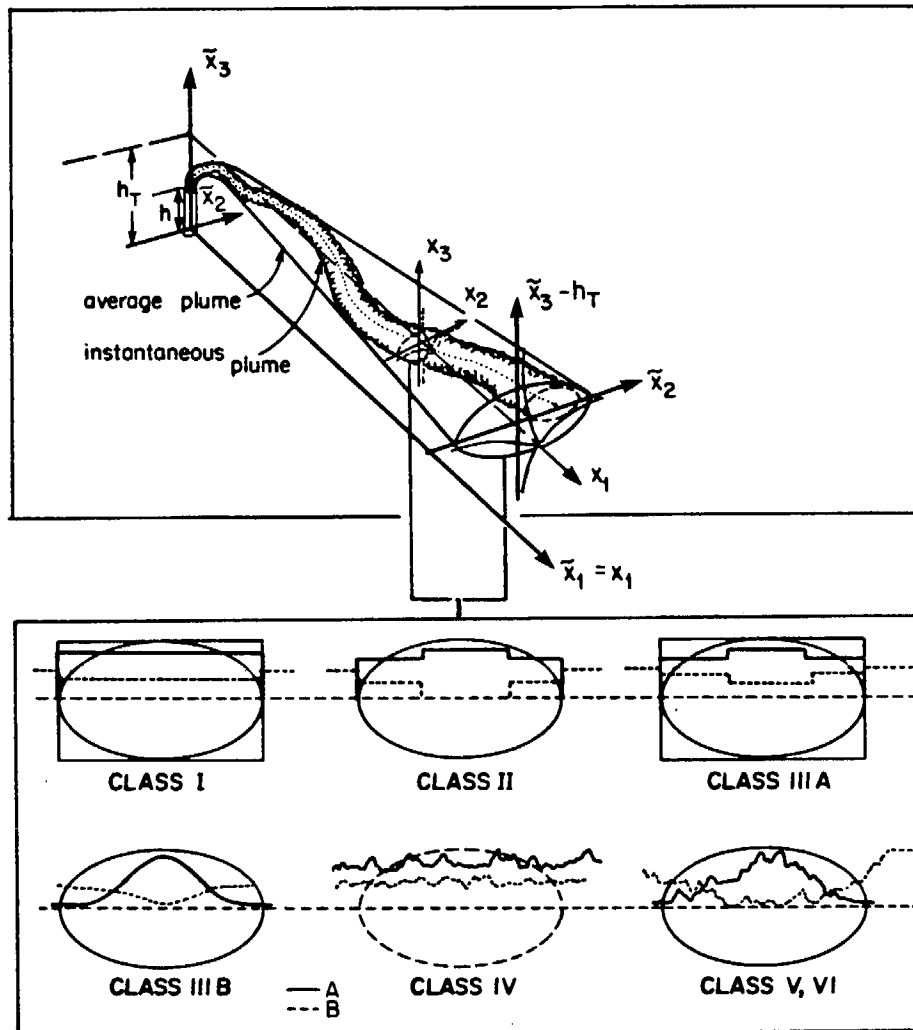


Figure 1-4
Schematic Representation
of the Basic Characteristics of Existing Reactive Plume Models
(according to the classification of Section 3)

The expanding plume is identified as a special control volume inside the atmospheric boundary layer (with the exception of the models of Class IV that consider uniform values of mean concentrations over the entire boundary layer), corresponding to either instantaneous plume realizations or (more often) to the time averaged envelope. (For models relevant to instantaneous realizations the mean concentrations must be ensemble averages and they can be in steady state only with respect to a frame of reference that follows the meandering centerline.) The cross-wind section of the plume is usually assumed to have elliptical shape (or rectangular in some of the models of Class I and IIIA); concentration profiles of the emitted and the ambient species (A and B respectively) that are typical in the various models are shown: Classes I to IIIB ignore the state of micromixing (local fluctuations) and assume profiles that are uniform (Class I), sectionally uniform (Class II, IIIA) or Gaussian (Class IIIB). Class IV takes into account fine scale fluctuations but ignores variations in the mean profiles. Finally Class V (and VI) consider the effects of both macromixing and micromixing.

by Freiberg (1976, 1978) who studied the oxidation of SO_2 in plumes. The model for the $\text{NO-NO}_2\text{-O}_3$ allows for turbulent exchange of material between adjacent rings. As far as the chemistry is concerned, it is assumed to be sufficiently slow so as not to be influenced by fine scale turbulent fluctuations.

Peters and Richards (1977) developed a model that belongs in Class IIIB. They assumed Gaussian profiles of concentration inside the plume and infinite rate chemistry and neglected completely concentration fluctuations. In order to obtain concentration profiles of the reactive species (reactants and products) they considered the transport of a conserved scalar (e.g., of a stoichiometric invariant of the reactive system). The transport equation of the conserved scalar is linear (no reaction term) and results in a Gaussian profile. Then the equilibrium relation (which is assumed to hold for mean concentration values since fluctuations are neglected) is used to obtain the reactive species concentrations. Although certain limitations of the atmospheric diffusion equation (see previous sections) were ignored, even so this model was a step beyond the perfectly mixed box models. White (1977) used the same principles to analyze the significance of experimental measurements.

Another model in Class III is that applied by Hegg et al. (1977), also in the analysis of experimental measurements. They assumed the reaction localized in the zone of highest concentration gradients and developed approximate schemes to obtain estimates of the time evolution of the reaction.

Class IV

Atmospheric fluctuations models (No consideration of mean concentration gradients): Donaldson and Hilst (1972), Bilger (1978), Kewley (1980), and Shu et al. (1978).

The studies of Donaldson and Hilst, Bilger, and Kewley refer to the effect of turbulent fluctuations on the nonlinear chemistry of a macroscopically mixed atmospheric volume where mean concentrations are uniform. Donaldson and Hilst (1972) were the first to show quantitatively the importance of fine scale fluctuations on nonlinear atmospheric chemistry. Bilger (1978) and Kewley (1980) used a version of

the "probability density of conserved scalars approach" to study the nature of the NO-O₃-NO₂ photostationary state, providing insight on the actual behavior of the atmospheric reactive systems in a state of incomplete mixing. Lamb (1976), Shu (1976) and Shu et al. (1978) considered a source of NO in a background environment containing O₃, neglecting mean concentration gradients and averaging their governing equations over cross-sections of the control volume.

Class V

Models that account for both mean field gradients and fine fluctuations: Hilst et al. (1973), Borghi (1974), Donaldson and Varma (1976) and Kewley (1978)

The works of Borghi (1974) and Donaldson and Varma (1976) are representative of how models employed in combustion aerodynamics can be applied to atmospheric problems involving strongly localized sources. These models consider mean field gradients and treat the fluctuations terms by direct (higher order) closure schemes. Although these approaches are very informative, the models are complex, often involving higher order closure schemes, and formulated for specific conditions. Thus they cannot be considered as appropriate for routine use in atmospheric applications.

A simplified adaptation of the approaches used in combustion modeling to the atmospheric plume problem was presented by Kewley (1978) based mainly on the work of Bilger (1978). However the assumptions involved in certain steps of its formulation, although valid for the fluid mechanics of combustion devices, are definitely

inappropriate for atmospheric conditions. (*)

Class VI

Probability density evolution formulations: O'Brien et al. (1976), Dopazo (1976), and O'Brien (1981).

This final class is included here for completeness; it consists of models that—at least in principle—attempt a complete characterization of the reacting system through estimation of the probability densities of the concentrations of all participating species. Evolution equations (based on methods from statistical mechanics) are constructed for the probability densities. However the works in this class are not yet in a form that would have practical use in atmospheric applications.

(*) The model of Kewley (1978) is a tractable formulation directly relating to atmospheric point source plumes (and in particular the ozone-nitrogen oxides system) that treats both mean concentration gradients and correlations of concentrations fluctuations. The method used to treat the fluctuations problem is a conserved scalar approach and is based on the assumption of infinite rate chemistry and pointwise equilibrium of the ozone-nitrogen oxides system wherever the reactants are mixed at the molecular level. There are however various weak points (besides this assumption of equilibrium) in the formulation of the model and the estimation of the parameters that are used. For example the common atmospheric diffusion equation is used as a starting point without consideration of time averaging effects and thus the transport closure approximation employed is not an appropriate one. Furthermore the variance of the concentration of an inert scalar, which accounts for local fluctuation effects by being used as a parameter in a clipped Gaussian probability distribution that is assumed to describe the conserved scalar field, is estimated on the basis of assumptions borrowed from the combustion literature that are not valid in atmospheric situations (see Chapter 5 for details). Of course even a better estimate of this variance would not help the situation that much, since, according to the preceding formulation of the model, the fluctuations would not be fluctuations about the correct quantity. Nevertheless, despite its points of invalidity this model is a rather simple approach that provides a qualitative understanding of certain of the phenomena that take place in a reactive plume.

1.6 CONCLUSIONS

The introductory analysis presented here showed that the evolution of systems of reactive pollutants in point source atmospheric plumes is determined in general by the combined action of both dispersive and reactive phenomena. These phenomena can lead to very complex physical situations as a consequence of the coupling of fast nonlinear kinetic rates with the turbulent nature of the flow field in which the reactions take place and the strongly localized character of the source.

All currently available theoretical studies of reactive plumes simplify – to different levels – the description of the complex system by introducing drastic assumptions, often wrong or misleading, about the importance and the nature of the coupling of the various interacting phenomena.

This first chapter considered both the nature of the reactive plume problem and the state of current research revealing the points that have not yet been treated properly; in the following we present the structure of a model that attempts to consider all the important aspects of the complex physical situation on the basis of explicitly stated assumptions.

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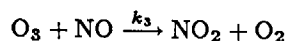
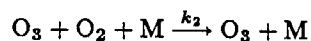
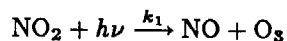
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APPENDIX A1.1

Simple Models
for Plume Mixing and Chemistry

The problem of release of species *A* in a background containing *B* (equations (1.3-1) to (1.3-5)) is often treated in atmospheric modeling practice by very simple methods. The most important example of this problem concerns the NO - NO₂ - O₃ system



(see also Chapter 3) and most applications have focused on it.

Thus, one approach is to treat the reaction between NO and O₃, that produces NO₂, as a pseudo-linear step by assuming that the background O₃ concentration remains uniform and constant everywhere, which essentially means that dispersion processes are so much faster than chemical processes that are able to instantaneously "recover" all the ozone that is depleted by reaction inside the plume (see Builtjes, 1983). This method accounts for macromixing only through the non-uniform distribution (Gaussian) of NO_x and ignores completely any micromixing effects. Thus the NO₂ produced by the third of the above reactions at any point will be given by

$$c_{\text{NO}_2} = c_{\text{NO}_x} [1 - \exp(-k_3 c_{\text{O}_3}^b)]$$

In another approach, that (instead of assuming infinite rate of "recovery" of chemically depleted ozone) considers completely uniform mixing inside every cross-section of the plume and equilibrium of the NO - NO₂ - O₃ system, McRae et al. (1982) formulated nitrogen and excess oxygen balance as follows:

Nitrogen:

$$\begin{aligned} c_{\text{NO}_x}(t) &= c_{\text{NO}_2}(t) + c_{\text{NO}}(t) \\ &= D(t)c_{\text{NO}_x}(0) + [1 - D(t)]c_{\text{NO}_x}^b \end{aligned} \quad (\text{A1.1} - 1)$$

Excess Oxygen (ignoring $O(^3P)$):

$$\begin{aligned} c_{O_x}(t) &= c_{NO_2}(t) + c_{O_3}(t) \\ &= D(t)[c_{NO_2}(0) + c_{O_3}(0) + [1 - D(t)](c_{NO_2}^b + c_{O_3}^b)] \end{aligned} \quad (A1.1 - 2)$$

In those expressions $D(t)$ refers to the plume dilution at time t , $c_{NO_2}(0)$ to the stack concentrations and the superscript "b" to the background values. The dilution is defined in terms of the change in the plume cross section area as a function of time. If the initial transverse area is A_0 and becomes $A(t)$ at some later time, t , then

$$D(t) = \frac{A_0}{A(t)} \quad (A1.1 - 3)$$

Thus there is a simple relation between the dilution and the growth of a cross-sectional segment of unit thickness:

$$\frac{1}{A(t)} \frac{dA(t)}{dt} = \frac{1}{D(t)} \frac{dD(t)}{dt} \quad (A1.1 - 4)$$

In addition to the dilution $D(t)$, the change in cross section area can be expressed in terms of the dispersion coefficients, σ_y and σ_x ,

$$\frac{1}{A(t)} \frac{dA(t)}{dt} = \frac{1}{\sigma_y \sigma_x} \frac{d\sigma_y d\sigma_x}{dt} \quad (A1.1 - 5)$$

If the ozone concentration in the source gases is negligible the excess oxygen balance can be written in the form

$$c_{O_3}(t) = c_A - c_{NO_2}(t) \quad (A1.1 - 6)$$

where

$$c_A = D(t)c_{NO_2}(0) + [1 - D(t)](c_{NO_2}^b + c_{O_3}^b) \quad (A1.1 - 7)$$

Then, writing the NO concentration as

$$c_{NO}(t) = c_B - c_{NO_2}(t) \quad (A1.1 - 8)$$

where

$$c_B = D(t)c_{NO_2}(0) + [1 - D(t)]c_{NO_2}^b \quad (A1.1 - 9)$$

one can utilize the equilibrium relation

$$c_{NO_2} = \frac{k_3}{k_1} c_{NO} c_{O_3} \quad (A1.1 - 10)$$

to obtain a quadratic expression for c_{NO_2} the only physically realistic solution of which is

$$c_{NO_2}(t) = \frac{1}{2} \left\{ \left(c_A + c_B + \frac{k_1}{k_3} \right) - \left[\left(c_A + c_B + \frac{k_1}{k_3} \right)^2 - 4c_A c_B \right]^{1/2} \right\} \quad (A1.1 - 11)$$

The variables c_A, c_B can be calculated from measurements of c_{NO}/c_{NO_x} in the stack exhaust, the dilution, and the background concentration of NO, NO₂, and O₃.

Thus we see how the assumptions of uniform mixing (in a reduced and expanding volume) and infinitely fast reaction are combined to obtain a very simple result (but actually highly unrealistic) of conversion in the NO - NO₂ - O₃ system.

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APPENDIX A1.2

Selected Plume Models

This Appendix contains a list of selected "Plume Models" (some of which take into account plume chemistry and other processes such as surface deposition, rain washout etc.) that are available in the public domain and have found wide application during the last decade. Most of them rely on the Gaussian plume concept; other formulations include applications of K-theory (either in a Lagrangian Trajectory or in an Eulerian Grid framework) or 2nd order closure methods. The majority of the models focuses on inert dispersion and linear removal mechanisms; among the models listed only IMPACT, PLMSTAR, RPM and TRACE take into account nonlinear chemistry. (However only RPM attempts to conform to the requirement of working with instantaneous plume statistics). Furthermore, only macromixing is included in these models; the interaction of turbulence and chemistry is ignored.

Some basic features of each model are listed as a brief description of its structure and capabilities; however it must be emphasized that some of these features may have been altered in more recent versions of the models. Thus this list is basically intended only to be indicative of the variety of approaches commonly employed in plume modeling. For further information, references and comparative discussion of plume models see Turner (1979), Benarie (1980), Liu et al. (1982), Burton et al. (1983) and Weber and Garrett (1984).

ADPIC

Lawrence Livermore Laboratory
University of California
Livermore, CA 94550

(R. Lange)

Comments: ADPIC is a three-dimensional Lagrangian particle model (10^4 cells, 2×10^4 particles, 1 km/50m horizontal/vertical resolution); it calculates hourly averaged concentrations. The wind field is determined by the MATTHEW model (inverse-square-weighting for surface wind data; vertical extrapolation via mass conservation principle and a stability dependent power law; algorithm for minimization of divergence of wind field that takes into account the underlying terrain).

- Fluid particles released from a source follow a Lagrangian trajectory under the influence of the prevailing wind and a pseudoveLOCITY representing turbulent diffusion. Each particle is tracked on an Eulerian grid, and the concentrations are computed by counting the total number of particles in a fluid cell. The horizontal dispersion coefficient is calculated using horizontal wind statistics; the vertical dispersion coefficient is assumed to obey a linear, height-dependent, relationship through the constant flux layer; both are functions of the distance from the source. Numerical solution is obtained by a modified particle in cell method.
- ADPIC considers chemically inert species but can be readily adapted to handle a linear chemical reaction; it treats surface deposition (flux proportional to product of surface concentration and deposition velocity) and washout and rainout (rate determined by product of concentration, rainfall rate, and a washout efficiency coefficient.)

AQSTM

*Illinois Environmental Protection Agency
Air Resources Analysis Section
2240 Churchill Road
Springfield, IL 62706*

Comments: AQSTM is a Gaussian model that estimates short term (1 to 24 hr avgs) inert species concentrations from multiple (up to 200) point sources. It takes into account plume rise (Briggs, post-1970 formulas) and inversion breakup, vertical wind variation (power law approximation), and provides an adjustment for non-flat terrain.

- The horizontal concentration profile is Gaussian; the vertical is initially Gaussian and finally uniformly mixed; power-law approximations to Pasquill-Gifford dispersion parameters (with sampling time correction) are used.*
- The dispersing species are assumed completely inert (no chemical or physical removal processes).*

ARAP

*Aeronautical Research Associates
of Princeton, Inc.
P.O. Box 2229
50 Washington Road
Princeton, NJ 08530
(W. S. Lewellen, C. duP. Donaldson)*

Comments: ARAP is a complex second-order-closure model that basically addresses the buoyant plume problem. It simulates evolution (in the near field) of plumes (either momentum or buoyancy dominated) into either a quiescent or windy atmosphere with stable, neutral and unstable stratification. ARAP is essentially a straightforward numerical scheme for plume rise (see Chapter 7).

ATM

Oakridge National Laboratory
Oakridge, TN 37830
(W. M. Culkowski, M. R. Patterson)

Comments: ATM is a discrete Gaussian model for point, line and area sources that estimates concentrations averaged over user-specified periods (larger than 1 hr). It is formulated for constant wind, flat terrain, and accepts user-specified plume rise.

- Horizontal concentration distribution is assumed uniform in each wind sector (22.5° sector averaging). Pasquill-Gifford-Turner and Hosker-Briggs-Smith dispersion coefficients (for distances up to 10 km and between 10 and 50 km respectively) are used for vertical dispersion.
- No chemical processes are considered. Dry deposition is treated through an effective source approach ("tilted plume approximation").

ARGONNE

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
(G. L. Mellor, T. Yamada)

Comments: ARGONNE is a second-order-closure model intended to simulate the behavior of buoyant plumes from large cooling ponds, basically on a mesoscale range.

BPM

Systems Applications, Inc.

101 Lucas Valley Road

San Rafael, CA 94903

(M. K. Liu, D. Durran, P. Mundkur M.

A. Yocke, J. Ames)

Comments: BPM is a two-dimensional model operating in two alternative modes (it either adopts an Eulerian approach with an Eulerian coordinate system spanning the downwind and vertical directions, or a trajectory approach with the cells spanning the crosswind and vertical direction). It employs K theory and calculates steady state concentrations (8×10^2 cells, 50m/30m horizontal/vertical resolution). BPM contains conservation equations for pollutant concentration and total mass as well as for momentum and energy; thus the wind fields are calculated internally.

- Horizontal and vertical eddy diffusivities are assumed equal; they are functions of the height (and boundary layer parameters) only.*
- BPM considers inert species only (no removal mechanisms, either physical or chemical).*
- Numerical solution is obtained through fractional steps with upstream-differencing scheme.*

CDM/CDMQC

U.S. Environmental Protection Agency

Office of Research and Development

Research Triangle Park, NC 27711

(A. D. Busse, J. R. Zimmerman)

Comments: CDM is a kinematic model that estimates either short term (1 to 24 hr) or long term (1 mo to 1 yr) concentration averages from point and area sources. It accounts for plume rise from point sources (Briggs, pro 1970 formulas) and vertical wind variation (power law profile). It is formulated only for flat terrain.

- Concentration distribution is assumed uniform in each wind sector. Power law approximations for Pasquill-Gifford dispersion coefficients are used. Algorithms for estimating existence of stack downwash effects and vertical depth of the well mixed plume.*
- The model can estimate constant exponential decay with user-assigned half life.*

CRSTER

*U.S. Environmental Protection Agency
Office of Air Quality Planning
and Standards*

Research Triangle Park, NC 27711

(J. H. Novak, D. B. Turner, J. R. Zimmerman)

Comments: CRSTER is a Gaussian model; it estimates concentrations averaged over either short term (1 hr to 12 hr) periods or over a year. It estimates plume rise (Briggs, post 1970 formulas) and takes into account vertical wind variation (power law extrapolation). The terrain is assumed flat.

- Pasquill-Gifford-Turner dispersion coefficients are used to estimate horizontal and vertical dispersion. Vertical dispersion is constrained by ground surface and inversion base (multiple reflection); concentration is finally assumed uniform in the vertical.*

- No removal mechanisms are considered.*

GEM

Science Applications, Inc.

875 Westlake Boulevard

Suite 212

Westlake Village, CA 91361

(A. Fabrick, R. Sklarew, J. Wilson)

Comments: GEM is a kinematic model for hourly averaged concentrations from a single point source. Plume rise is estimated by Briggs (pro 1970 formulas), but the user must specify the appropriate formula. Wind speed may be provided by the numerical wind model WEST. Nonflat terrain can be considered.

- Concentration is assumed to be Gaussian in the near field (vertically uniform in the far field); the user specifies dispersion coefficients of his own choice or from a variety of model provided options.*

- Only linear chemical processes can be taken into account.*

IMPACT

Science Applications, Inc.
875 Westlake Boulevard,
Suite 212
Westlake Village, CA 91361
(A. Fabrick, R. Sklarew, J. Taft,
J. Wilson)

Comments: *IMPACT* is a (three-dimensional) Eulerian grid model (10^4 cells; 1 km/50 m horizontal/vertical resolution; hourly averaged concentrations) employing *K* theory. The wind field is obtained by a divergence minimization algorithm (that takes into account the underlying terrain).

- Vertical eddy diffusivities are calculated as functions of height and boundary layer parameters; horizontal eddy diffusivities are obtained from the vertical ones through multiplication by a stability-dependent coefficient.
- *IMPACT* uses a version of the Hecht-Seinfeld-Dodge mechanism for the chemical kinetics. Surface deposition is calculated by assuming the removal flux proportional to the product of surface concentration and a deposition velocity.
- Numerical solution is obtained through fractional steps (with second order flux correction) method.

INTERA

Intera Environmental Consultants
2000 West Loop South, Suite 2200
Houston, TX 77027
(R. B. Lanz, K. H. Coats, C. Kloepper)

Comments: *INTERA* is a (three-dimensional) Eulerian grid model (10^4 cells; variable resolution, hourly-averaged concentrations) employing *K* theory. The wind field is obtained by a divergence minimization algorithm (flat terrain assumed).

- Horizontal diffusivities are assumed to be simple exponential function of height only (involving stability dependent exponents); vertical eddy diffusivities are then calculated through multiplication by a stability-dependent coefficient.
- Only a linear reaction and surface deposition can be treated by *INTERA*.
- Numerical solution is obtained through an upstream differencing scheme.

ISC/ISCST

H. E. Cramer Company, Inc.
University of Utah Research Park
P. O. Box 8049
Salt Lake City, UT 84108
(J. F. Bowers, J. R. Bjorklund,
C. S. Cheney)

Comments: *ISC/ISCST* is a kinematic model for point, line, area and volume sources; the averaging time is user-specified, up to 24 hours. The model estimates plume rise (Briggs, post 1970 formulas) and takes into account vertical variation in horizontal wind speed (power law extrapolation).

- Pasquill-Gifford-Turner dispersion coefficients are used for point sources without effects of building wakes; a modified set of coefficients is used for volume sources and point sources with effects of building wakes. (For $x < 100$ m no treatment is provided). Perfect reflection from inversion base and ground surface and finally uniform mixing in the vertical is assumed.
- Only linear processes can be treated.

MESOGRID

Environmental Research and Technology,
Inc.
696 Virginia Road
Concord, MA 01742
(C. S. Morris, C. W. Benkley, A. Bass)

Comments: *MESOGRID* is a three-dimensional Eulerian grid model (2×10^5 cells; variable resolution; hourly or longer averaged concentrations) employing K theory. The wind field is assumed two-dimensional; observed winds are iteratively adjusted to remove the excessive divergence in the interpolated wind field. *MESOGRID* uses a special horizontal treatment that is more appropriate to mesoscale problems: vertical advection is assumed much smaller than vertical diffusion whereas horizontal advection is assumed to be much smaller than horizontal advection.

- *MESOGRID* does not use a horizontal eddy diffusivity; its vertical eddy diffusivity is calculated through an algorithm, similar to the ones employed in IMPACT, PDM and RADM, based on the similarity theory for the planetary boundary layer.
- *MESOGRID* was specifically designed to estimate atmospheric conversion of SO_2 to sulfate; surface deposition is also included.
- Numerical solution by the method of moments horizontally; forward-centered differencing vertically.

MESOPUFF

*Environmental Research and Technology,
Inc.*

*696 Virginia Road
Concord, MA 01742*

(C. W. Benkley, A. Bass)

Comments: MESOPUFF is a regional scale kinematic model for point sources that provides concentrations averaged over a user-specified period (with minimum of 1 hour). It takes into account plume rise (Briggs, pro 1970 formulas) and fumigation. It uses gridded wind speed values input at each update interval; the whole puff is advected depending on winds at puff center. The terrain is assumed flat.

- PGT coefficients are used for vertical and horizontal dispersion for distances less than 100 km; for larger distances Heffter's dispersion coefficients are used. The user specifies condition of either multiple reflection or uniform mixing below the inversion base.*
- The model treats linear decay of SO_2 to SO_4^{-2} and dry deposition of SO_2 and SO_4^{-2} .*

MPTEP

*U.S. Environmental Protection Agency
Meteorology and Assessment Division
Research Triangle Park, NC 27711
(T. E. Pierce, D. B. Turner)*

Comments: MPTEP is a kinematic point source model providing averages over 1 to 24 hours. Plume rise is treated through Briggs formulas. An adjustment for non-flat terrain is provided.

- PGT horizontal and vertical coefficients are used; finally uniform mixing is assumed in the vertical.*
- Constant exponential decay with user-assigned half-life.*

MSDM

*Lawrence Livermore Laboratory
University of California
Livermore, CA 94550
(D. L. Ermak, R. A. Nyholm)*

Comments: MSDM is a kinematic model for point sources providing hourly, seasonal or annual concentration averages. Plume rise is treated by empirical formulas and vertical wind variation through a power law extrapolation.

- Coefficients based on the Pasquill-Gifford scheme are used. Horizontal dispersion is corrected for initial dilution effects. Initially multiple reflection and finally uniform mixing is assumed in the vertical. In the long term mode sector averaging is used.*
- Linear chemistry (chains of up to three reactions) and dry deposition and gravitational settling (proportional to the ground level atmospheric concentration) are treated.*

MULTIMAX

*Shell Development Company
Westhollow Research Center
P.O. Box 1380
Houston, TX 77001
(J. H. Moser –
modified by Koss and Condrey
at Tennessee Valley Authority)*

Comments: MULTIMAX is a kinematic model for point sources providing 1-, 3-, 24- hour and annual concentration averages. It uses Briggs formulas for plume rise and power-law extrapolation for the vertical variation in wind speed.

- Pasquill-Gifford-Turner horizontal and vertical coefficients are used with optional sampling time correction. Vertical dispersion is assumed constrained by ground surface and inversion base (multiple reflection).*
- Only linear processes can be handled.*

PAL

U. S. Environmental Protection Agency
Meteorology and Assessment Division
Research Triangle Park, NC 27711
(W. B. Peterson)

Comments: PAL is a kinematic model that calculates 1 to 24 hour-averages of concentrations from point, area and four types of horizontal line sources (straight and curved). Plume rise is taken (optionally) into account through Briggs (post 1970) formulas. A power law extrapolation is used for the vertical wind speed. The terrain is assumed flat.

- PGT dispersion coefficients are used; both horizontal and vertical coefficients are corrected for initial dilution effects. Multiple reflection and finally uniform mixing is assumed in the vertical.
- No removal processes are considered.

PDM

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903
(M. K. Liu, D. Durran, P. Mundkur,
M. A. Yocke, J. Ames)

Comments: PDM is a hybrid three-dimensional, Eulerian, grid and trajectory puff model (a Gaussian puff module is incorporated in an Eulerian grid model to enhance the spatial resolution near strong point sources). It calculates hourly averaged concentrations (10^4 cells, 1 km/50 m horizontal/vertical resolution). The wind field is determined either (a) by interpolating observed surface winds—assumed constant with height—and then estimating vertical winds in terms of the horizontal divergence, or (b) by employing a wind model that is based on the mass-consistency principle.

- The horizontal eddy diffusivity is a user-specified constant. The vertical diffusivity is assumed a function of height (and boundary layer parameters) and is calculated through an algorithm that utilizes atmospheric similarity theory.
- PDM calculates atmospheric conversion of SO_2 to sulfate; surface deposition is also included.
- Numerical solution through a fractional steps (flux corrected) method.

PLMSTAR

Environmental Research and Technology, Inc.

696 Virginia Road

Concord, MA 01742

(F.W. Lurmann et al.)

Comments: PLMSTAR is a Lagrangian trajectory model estimating short term averages of concentration (variable horizontal and vertical resolution provided by a two-dimensional wall of cells advected by the mean wind). Wind field is determined by a divergence minimization algorithm; the validity of the trajectory approximation is also checked under the specific conditions relevant to the calculations.

- Vertical eddy diffusivities are functions of height and (stability dependent) boundary layer parameters; the horizontal diffusivities are then calculated by multiplying with a stability dependent coefficient. Alternatively, eddy diffusivities for dispersion from strong point sources are calculated in terms of (absolute) dispersion parameters that are functions of the travel time from the source.*
- A reduced form of the ERT photochemical mechanism describes plume chemistry.*
- Numerical solution is obtained by a scheme that discriminates between stiff and non-stiff ordinary differential equations.*

PTDIS

U. S. Environmental Protection Agency

Meteorology Assessment Division

Research Triangle Park, NC 27711

(D. B. Turner, A. D. Busse)

Comments: PTDIS is a kinematic model for a single point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.

- PGT horizontal and vertical dispersion coefficients are used; multiple reflection is assumed in the vertical.*
- No removal processes are considered.*

PTMAX

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, A. D. Busse)

Comments: *PTMAX* is a kinematic model for a single point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.

- PGT horizontal and vertical dispersion coefficients are used; vertical dispersion is constrained by ground reflection only.
- No removal processes are considered.

PTMTP

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, A. D. Busse)

Comments: *PTMTP* is a kinematic model for multiple (up to 25) point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.

- PGT horizontal and vertical dispersion coefficients are used; multiple reflection is assumed in the vertical.
- No removal processes are considered.

RADM

*Dames and Moore
Advanced Technology Group
1100 Glendon Avenue, Suite 1000
Los Angeles, CA 90024
(A. K. Runchal, W. R. Goodin,
K. J. Richmond)*

Comments: RADM is a three-dimensional Lagrangian particle model (2×10^4 particles; hourly averaged concentrations; variable resolution) utilizing K theory. First the probability of finding a particle at a given location is calculated and then the concentration at a given location is determined from the distribution of particles in an Eulerian framework. The wind field is obtained by a divergence minimization algorithm (that takes into account the influences of both the underlying terrain and the vertical temperature gradient.)

- Vertical eddy diffusivities are a function of height and (stability dependent) boundary layer parameters; horizontal eddy diffusivities are assumed functions of stability dependent boundary layer parameters only. Calculations are based on a random walk approach.*
- RADM estimates conversion of SO_2 to sulfate. Surface deposition is included.*

RAM

*U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, J. H. Novak)*

Comments: RAM is a kinematic model for point and area sources. It calculates 1 to 24 hr averages. Plume rise is treated by Briggs (post 1970) formulas and wind speed variation in the vertical by power law extrapolation. The terrain is assumed flat.

- PGT horizontal and vertical coefficients are used for dispersion over rural areas; Briggs coefficients are used for urban areas. Multiple reflection is assumed in the vertical.*
- Constant exponential decay with user assigned half-life.*

RPM

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903
(M. K. Liu, D. A. Stewart,
T.W. Tesche)

Comments: RPM is a two-dimensional trajectory puff model based on the Gaussian plume concept. A wall of rectangular vertical cells (perpendicular to the plume centerline) expands downwind, its total dimensions being four times the values of the relative dispersion parameters. Mass is reapportioned in the cells through an artificial diffusion mechanism.

- *Horizontal and vertical dispersion parameters that determine the cell wall size are assumed to be functions of the dispersion time. The McElroy-Pooler parameterization scheme is adopted to estimate absolute dispersion. Then relative dispersion parameters are just assumed to be 1.5 times smaller than the corresponding absolute dispersion parameters (for all atmospheric stability classes). Artificial diffusion coefficients are used to account for mass transfer between cells. All cells are assumed uniformly mixed; thus the model provides only horizontal resolution.*
- *Modified formulations of the Carbon-Bond Mechanism are adopted in the various versions of the RPM family of models.*
- *Numerical solution is obtained by schemes appropriate for the solution of the stiff ordinary differential equations that describe concentration evolution in each expanding cell.*

SCIM

GEOMET, Inc.
15 Firstfield Road
Gaithersburg, MD 20760
(R. C. Koch)

Comments: SCIM is a kinematic model for point and area sources. It calculates 1 hr to 1 yr averages. The model takes into account plume rise (Briggs, post 1970 formulas) and wind speed variation in the vertical (power-law extrapolation).

- *PGT dispersion coefficients are used for rural areas; McElroy coefficients are used for urban areas. Perfect ground reflection and finally uniform mixing is assumed in the vertical.*
- *Constant exponential decay with user assigned half-time.*

STRAM

*Battelle Pacific Northwest Laboratories
P.O. Box 99
Richland, WA 99352
(J. M. Hales, D. C. Powell, T. D. Fox)*

Comments: STRAM is a two-dimensional Lagrangian trajectory model (essentially a segmented Gaussian model, 5-20 cells; hourly or longer averaged concentrations, variable resolution). Each segment of the STRAM is mass-integrated in the cross-wind and vertical direction. The rate of change of the integrated pollutant mass is controlled by the difference between the upstream inflow and downstream outflow area-integrated mass flux. A combination of (volume-integrated) chemical reaction, washout, and source and sink terms, is also included in the mass balance equations. The wind field is determined by direct interpolation (only horizontal wind speeds are required). STRAM is intended for long range transport problems (distances larger than 10 km from the source).

- Horizontal and vertical dispersion parameters are assumed to be functions of the downwind distance along the trajectory, described by simple exponential laws and stability dependent coefficients (the horizontal dispersion parameter exponent is taken equal to 0.9; the corresponding exponent for the vertical dispersion is assumed stability dependent).*
- STRAM calculates atmospheric conversion of SO_2 to sulfate; surface deposition and washout-rainout are included.*
- Numerical calculations employ Gauss-Laguerre quadrature; second-order Runge-Kutta integration.*

TCM

Texas Air Control Board
6330 Hwy 290 East
Austin, TX 78723
(R. A. Porter, J. H. Christiansen)

Comments: TCM is a long term average (1 mo to 1 yr) model for point and area sources. Briggs plume rise equations under unstable or neutral conditions are used for all atmospheric conditions (only for the point sources). A power law is assumed for the vertical variation of the wind speed. The terrain is assumed flat.

- Uniform concentration distribution in the horizontal direction are assumed within each wind sector (22.5° sector averaging). Power-law approximation to Pasquill-Gifford curves are used for vertical dispersion; finally uniform mixing is assumed.
- Constant exponential decay with user assigned half-time.

TEM

Texas Air Control Board
6330 Hwy 290 East
Austin, TX 78723
(R. A. Porter, J. H. Christiansen)

Comments: TEM is a kinematic model providing short term (10-min, 30-min, 1-hr, 3-hr, 4-hr, 24-hr averages) concentration from multiple point (up to 300) and area (up to 200) sources. Briggs formulas are used to calculate plume rise and a power law extrapolation is used for wind variation in the vertical. The terrain is assumed flat.

- Power law approximations of Pasquill-Gifford coefficients are used; finally uniform mixing is assumed in the vertical.
- Constant exponential decay with user-assigned half-life.

TRACE

AMI

Applied Modeling, Inc.

Los Angeles

(K.T. Tran)

Comments: *TRACE* is a Lagrangian trajectory model providing short term averages of concentration (variable horizontal and vertical resolution of a two-dimensional wall of cells advected by the mean wind). Wind field is determined by a divergence minimization algorithm.

- Vertical eddy diffusivities are functions of height and (stability dependent) boundary layer parameters; the horizontal diffusivities are then calculated by multiplying with a stability dependent coefficient.
- The McRae-Seinfeld photochemical mechanism is employed for the description of the chemical kinetics.
- Numerical solution is obtained by a scheme that discriminates between stiff and non-stiff ordinary differential equations.

VALLEY

U. S. Environmental Protection Agency

Office of Air Quality Planning

and Standards

Research Triangle Park, NC 27711

(E. W. Burt)

Comments: *VALLEY* is a kinematic model that calculates 24 hr, seasonal, and annual averages of concentrations from multiple (up to 50) point sources. It estimates plume rise (Briggs, post 1970) formulas and assumes constant wind speed with height. An adjustment for non-flat terrain is included.

- Horizontally uniform concentration distribution is assumed in each wind sector (22.5° sector averaging). PGT coefficients (with near-ground source correction for urban areas) are used for the vertical dispersion. Multiple reflection and finally uniform mixing are assumed in the vertical.
- Constant exponential decay with user-assigned half-life.

**References
for Appendix A1.2**

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CHAPTER 2

THE TURBULENT REACTING PLUME MODEL (TRPM): STRUCTURE AND PARAMETERS

2.1 INTRODUCTION

In order to overcome deficiencies of currently available plume models, as they were described in Chapter 1, a new scheme, to be called the Turbulent Reacting Plume Model (TRPM), has been developed and is schematically presented in Figure 2-1 (page 67). The TRPM offers a comprehensive description of the evolution of atmospheric plumes, conforming to the requirement that models of nonlinear in-plume processes must:

- (i) be based on ensembles of instantaneous and not time averaged realizations of the plume (avoid temporal averaging),
- (ii) not ignore the existence of mean concentration gradients in the instantaneous plume cross sections (avoid spatial averaging), and
- (iii) include a scheme that estimates the effects of fine scale fluctuations on the chemical rates.

In this treatment, and at the present level of development of the TRPM, the focus is on the quantitative analysis of the *interaction* of mixing and chemical processes. The approach followed discriminates between fluid-mechanical phenomena that interact with nonlinear chemistry (relative or two-particle dispersion due to small scale turbulence of the background air, possibly aided by the initial plume buoyancy and

momentum) and phenomena that do not interact with chemistry (meandering, expected plume rise) and takes them into account separately.

The working model is a modular mathematical scheme that allows for alternative descriptions (at various levels of complexity) of the various processes involved in the reaction-dispersion phenomenon.

The core of the model is a "master module" that contains the differential evolution or algebraic local equations (depending on the assumptions appropriate for each specific system) for "progress variables" that describe the state of dispersion and reaction process. A new progress variable that utilizes spatially varying stoichiometry to reduce computational burden, and at the same time is a useful quantitative measure of the effect of mixing on reaction at each point, is introduced and used in this work; it is called the "*local phenomenal extent of reaction*" and the governing equations are formulated in terms of it. These equations represent the fundamental transport-reaction balances. They utilize

- (a) a first order closure scheme for the turbulent dispersion (modified K theory: modified in the sense that the K's used are not properties of the flow field but, at any "receptor point," of the specific source-receptor pair, and the solution is relevant to expected instantaneous values and not temporally and spatially averaged quantities), and
- (b) an indirect chemical closure scheme for the turbulent kinetic rates based on a "concentration field splitting" technique that accounts for the effect of fluctuations in the nonlinear terms. (For comparison calculations the model can ignore this effect and use conventional, non-turbulent kinetics.)

The calculations performed by the master module of the TRPM estimate expected pointwise concentrations of reactants and products inside the instantaneous plumes (relative to the center of mass of each cross-section). The required inputs for these calculations (to be called "inner level" parameters) are supplied by independent "peripheral modules" as follows:

- (a) Dispersion coefficients that account for relative dispersion processes alone: A new

iterative scheme that allows their estimation from observed atmospheric turbulence spectra has been formulated and is presented in Chapter 6. Alternatively available semi-empirical relations can also be used.

(b) The intensity of plume segregation (which measures completeness of fine scale mixing): This can be computed alternatively, from a first order closure numerical scheme for σ_c^2 , or from the analytical expressions provided by the "Localized Production of Fluctuations Model" which has been developed for the needs of this work and is presented in Chapter 5.

Another peripheral module provides the information needed for the a posteriori calculation of averaged, or instantaneous, fixed point concentrations (needed to connect the plume model with more extended air quality models) by determining its mean path and local time-averaged size through "outer level" parameters. These define a translating coordinate system attached to the instantaneous plume centerline (i.e., following its bulk bodily movements). Plume rise and meandering determine the position of this system. Meandering is modeled as a random (typically Gaussian) process through the fluid particle transition function of the turbulent field, and plume rise is simulated either by a comprehensive three-dimensional integral approximation scheme or, alternatively, by simple semi-empirical formulas.

The availability of alternative schemes for parameter estimation ensures flexibility of the overall formulation and allows control on the complexity of the working model and of the associated computational burden, in accordance with the quality of available inputs and the objective of the particular calculations. Application of the TRPM to the NO - NO₂ - NO₃ system of reactions, which is of particular importance in point-source atmospheric plumes, is presented in Chapter 3; comparison with available experimental data offers a satisfactory first evaluation of the model.

The following analysis focuses on the model problem described by equations (1.3-1) and (1.3-2) of Chapter 1, i.e. the second order reaction between the unpremixed species A (from the source) and B (from the background air). The objective is to transform the reaction-dispersion equation (1.3-6) in a solvable form via appropriate transport and chemical closure schemes, i.e. via a realistic parameterization of the turbulent fluctuation correlations appearing in equations (1.3-6) and (1.3-7).

2.2 BASIC ASSUMPTIONS AND APPROXIMATIONS

At the present stage of development of the TRPM it is assumed that the fine scale turbulence responsible for the phenomena of plume growth and entrainment is determined mainly by the fine scale dynamics of the ambient atmospheric flow field. Thus we neglect the effect that initial plume dynamics (buoyancy and momentum) may have on the evolution of the reactive system. The justification for this assumption is that in most practical cases the self-generated turbulence of the plume is a dominant factor in the mixing process only for travel times up to a few seconds for typical wind speeds (Csanady, 1973 - Section 6.12). Since the overall mixing of the plume with the background air will also be minimum during this stage of plume dispersion, it is therefore reasonable to conclude that no appreciable conversion of reactants to products has taken place in the initial phases that are dominated by the source dynamics. Naturally this assumption becomes more realistic in cases where initial buoyancy and momentum are actually small (as is the case in controlled wind tunnel experiments that can be utilized for initial model verification). If, however, the source effects are so intense that mixing at the initial phases of plume growth should be taken into account in a more precise way, then a first practical solution to this problem is to consider a virtual source at a sufficient distance upwind of the real source, such that background turbulence alone would have caused the same overall mixing at points downwind as self-generated turbulence acting for the actually traveled distances.

To meet the requirement that the governing equations must represent the *expected* instantaneous dynamics of the plume and not some time averaged envelope, we adopt a frame of reference with its origin always on the meandering centerline of the plume. A standard Galilean transformation is needed for the fixed frame equations to apply in the new coordinates. The mean concentration fields (*not* the corresponding stochastic fields) viewed from the moving frame are in a "true" steady state in the sense that

they remain invariant with respect to infinitesimal time shifts. A time averaged field viewed from a fixed position would be in steady state only for averaging times long enough to incorporate and "smooth out" meandering effects of various scales. Thus the steady state of the plume envelope as viewed from a ground observer is a different concept from the steady state that is considered here and that actually refers to isolated relative diffusion.

For a continuous steady release one has $\partial \langle \cdot \rangle / \partial t = 0$ in the meandering coordinates. For notational convenience it is subsequently assumed that all dependent and independent variables are defined in the moving frame. In this way random bodily movements of the plume are "extracted" from the mean mixing operator $\langle \mathcal{L}^M \rangle$, (modeled through a Lagrangian scheme) which still describes advection and relative turbulent as well as molecular diffusion phenomena. The assumption that this operator remains of the same form in the fixed and the randomly meandering frames is discussed in detail in Chapter 6 (by considering essentially the operator's Green's function), and is justified for the idealized case of point source and homogeneous-stationary turbulence; for more realistic (and therefore complicated) situations one expects this assumption to be valid for relatively *mild meandering*.

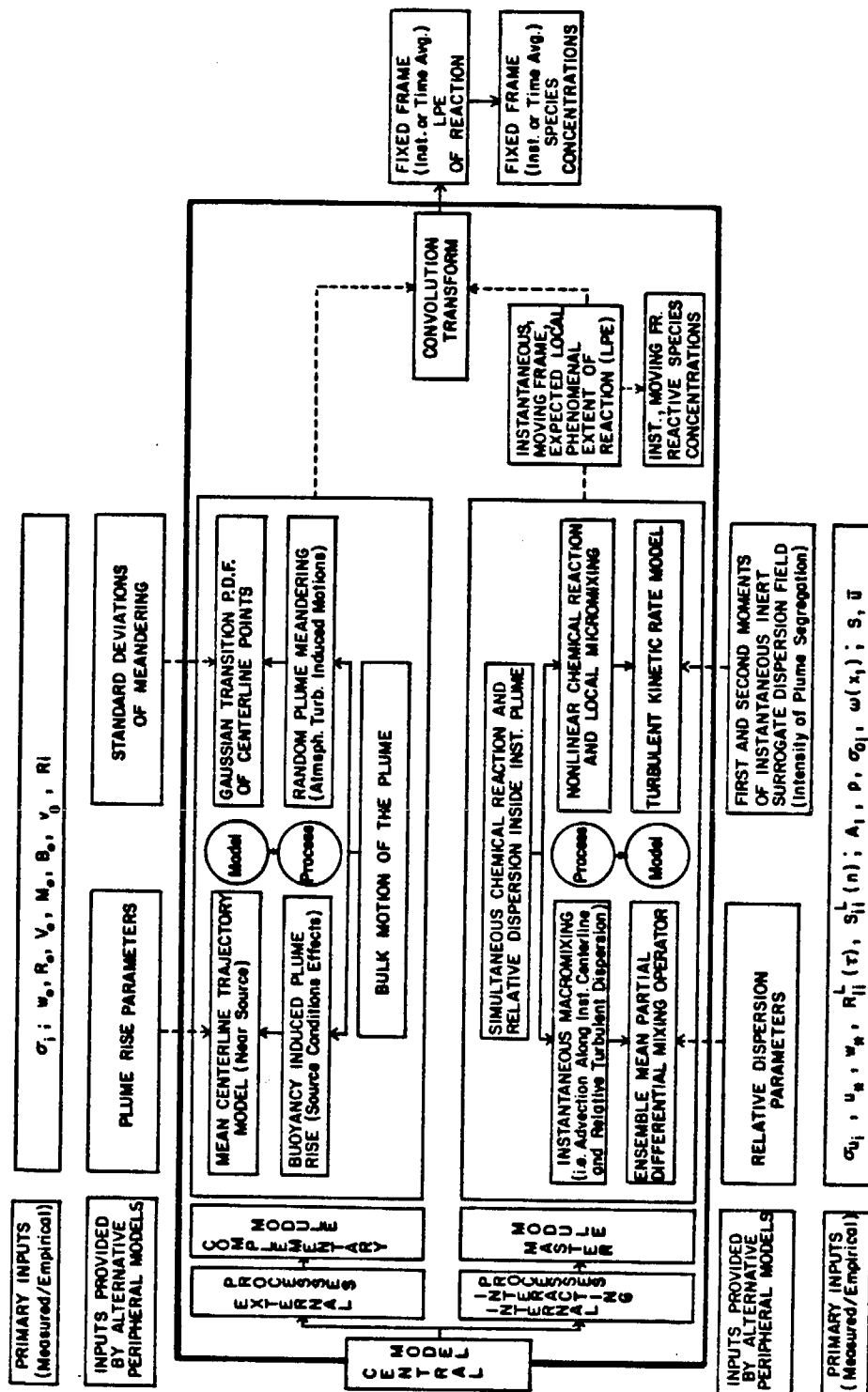


Figure 2-1
Structure of the Turbulent Reacting Plume Model (TRPM)

2.3 MODELING THE GOVERNING EQUATIONS: THE MIXING TERM

$\langle \mathcal{L}^M \rangle$ must be modeled in such a way that after the introduction of the closure approximation it still describes mean instantaneous realizations of the plume. Exclusively "fluid particle dispersion" will be associated with $\langle \mathcal{L}^M \rangle$ on the assumption that molecular diffusion is negligible in comparison to turbulent transport. Special attention must be given to this step. Molecular diffusion is by no means a "negligible" or unimportant phenomenon in the structure of the overall process. On the contrary, it may control the overall rates of chemical conversions. However, its major effect consists of *homogenizing* the mixture of plume gases and background air at local scales and not in transporting material macroscopically. Thus molecular diffusion affects the steady state distribution of fluctuations rather than of mean concentrations, which are determined by turbulent diffusion. In this sense we "neglect" the molecular diffusion term in the l.h.s. of equation (1.3-6); actually the effects of molecular diffusion will be *incorporated implicitly* in the r.h.s. of this equation, in a phenomenal kinetic rate that accounts for the effects of fine scale fluctuations.

The theoretical basis for the development of closure schemes that take into account the scale-dependent properties of the mixing process, and therefore reflect the *nonlocal* character of turbulent dispersion, is reviewed in the monograph of Leslie (1973 – Chapters 8 and 12) and in Monin and Yaglom (1975 – Section 24); more recent developments are discussed in Jiang (1985). These schemes lead to the development of integrodifferential equations for $\langle c \rangle$ (more exactly for the transition probability density of fluid particles) that involve the mixed space-time correlations of either Eulerian or Lagrangian velocity fields. However, the current formulation of the TRPM adopts the simplest version of this approach by utilizing a dispersion equation with "apparent" eddy diffusivities that depend on the travel time (see Csanady, 1973 – Section 3.8; Berlyand, 1975 – Section 2.6). A formal construction of this model

is possible, e.g. starting from Roberts' (1961) equation (equation 24.8 of Monin and Yaglom, 1975), and reducing it to a partial differential equation by assuming

- (i) velocity fields that are delta correlated in space (see also Runca et al., 1983), and
- (ii) that the fluid particles' positions constitute first order Markovian processes.

A more detailed discussion of the assumptions and problems associated with the apparent eddy diffusivities concept is presented in Chapter 6.

Introducing the eddy diffusivities in terms of the instantaneous plume description, i.e. as

$$K_i(t) = \frac{1}{2} \frac{\sigma_{R_i}^2}{dt} \quad (2.3 - 1)$$

where σ_{R_i} is the dispersion parameter for relative diffusion, the ensemble mean form of the mixing operator will be

$$\langle \mathcal{L}^M(\cdot) \rangle \simeq \mathcal{L}_K^M \langle \cdot \rangle = \frac{\partial \langle \cdot \rangle}{\partial t} + \langle u_i \rangle \frac{\partial \langle \cdot \rangle}{\partial x_i} - K_i \frac{\partial^2 \langle \cdot \rangle}{\partial x_i \partial x_i} \quad (2.3 - 2)$$

A further *optional* assumption in the TRPM is that of negligible turbulent diffusion in comparison to advection in the direction of mean wind speed (the common "slender plume approximation"). This assumption of no back-mixing implies that plume species will interact chemically only with the background air and not with plume material of different "age" (which is at a different stage of dilution and chemical conversion). Since recirculation eddies inside the plume will necessarily mix "fresh" effluent with "older" material, the validity of this approximation will depend on the magnitude of the mean wind speed and the atmospheric stability conditions.

Thus, for example, for steady and relatively strong mean wind speed \bar{u}_1 in the x_1 -direction, the mean mixing operator will be approximated by

$$\mathcal{L}_K^M \langle \cdot \rangle = \bar{u}_1 \frac{\partial \langle \cdot \rangle}{\partial x_1} - K_2(x_1) \frac{\partial^2 \langle \cdot \rangle}{\partial x_2^2} - K_3(x_1) \frac{\partial^2 \langle \cdot \rangle}{\partial x_3^2} \quad (2.3 - 3)$$

2.4 MODELING THE GOVERNING EQUATIONS: THE REACTION TERM

(a) The Chemical Closure Problem

Modeling the r.h.s. of equation (1.3-6), i.e. introducing a closure scheme for the second order turbulent kinetics, has been the explicit or implicit objective of an extensive amount of research in several fields of science and engineering; the relatively few and recent applications in the field of air pollution modeling were mentioned in the review of Chapter 1.

At this point one must realize that a knowledge of the fundamental concepts underlying the various approaches that have been proposed to provide closure to turbulent kinetics equations (and of the relative merits and limitations of these approaches) is a prerequisite in selecting the most appropriate method for a given application; for this reason a review and classification of existing modeling methods, with the focus on their potential applicability to the atmospheric plume problem, is presented in Chapter 4.

To summarize some basic ideas of Chapter 4, approaches that deal explicitly with global Eulerian statistical transport-reaction equations of the form of (1.3 - 3) and (1.3 - 6) can be classified as "direct", when correlations (or joint pdf's) of reacting species concentrations such as c_A , c_B are modeled directly through algebraic or differential equations, and as "indirect" or "mixing-reaction-decoupling" approaches, in which the quality of mixing (at both macroscopic and microscopic scales) is studied separately, in terms of some auxiliary variables, commonly called "conserved scalars", that are not affected by the chemical reaction, and is subsequently related to the observed phenomenal chemical rate.

The indirect closure method is presently at a better state of development and in general leads to more tractable schemes than direct methods; it was actually originated as early as 1928 (Burke and Schumann, 1928) and has often been reintroduced

since then (Hawthorne et al., 1949; Toor, 1962). In the case of infinitely fast ("instantaneous") reactions, closure is needed only for correlations or pdf's of the conserved scalars (e.g. Kewley's (1978) model). When the chemical rate is finite, parameterization of expressions involving both conserved scalars and reaction sensitive variables is also necessary. Such an approach was adopted by Shu (1976), Lamb (1976), and Lamb and Shu (1978); however, their analysis was restricted to macroscopically cross-sectionally uniform concentration fields and thus limited the applicability of their model to one-dimensional problems (i.e. considering variations of mean concentrations only in one, spatial or temporal, dimension).

A general formulation of the method, in a way that holds for pointwise defined instantaneous concentrations in arbitrary, non-uniform, fields is briefly presented next; some further discussion can be found in Chapter 4 and in Appendix A4.1.

(b) *The "Concentration Field Splitting" Method*

Let $c_A^I(\mathbf{x}, t)$, $c_B^I(\mathbf{x}, t)$ be the hypothetical concentrations of A and B that would exist at the space-time point (\mathbf{x}, t) if they did not react with each other but, still, were transported in the field by exactly the same molecular and convective mechanisms. We can define these new variables as concentrations of fictitious *inert surrogates* A^I , B^I , of A and B . c_A , c_B as well as c_A^I , c_B^I at any (\mathbf{x}, t) are random variables. The approach proposed in this work accounts for the possible states of mixing of the two species by viewing each of the above concentration fields not only as random functions of (\mathbf{x}, t) but also as *functionals* of the entire ensembles of realizations of the inert surrogate of their "mixing partners" at (\mathbf{x}, t) . Indeed, the possible micromixing states of, say, A or A^I at any point depend on the probabilistic characteristics of the concentration of B^I at this point. Thus $c_A(\mathbf{x}, t)$ and $c_A^I(\mathbf{x}, t)$ are functionals of the ensemble of all possible values of $c_B^I(\mathbf{x}, t)$. This dependence is expressed formally through the following integral representation of each random realization of, say, $c_A(\mathbf{x}, t)$:

$$c_A(\mathbf{x}, t; [c_B^I(\mathbf{x}, t) = \gamma_B^I]) = \int c_A(\mathbf{x}, t; [c_B^I]) \delta(\gamma_B^I - c_B^I(\mathbf{x}, t)) dc_B^I \quad (2.4 - 1)$$

Then, defining

$$a = c_A(\mathbf{x}, t; [c_B^I = 0]), \quad \alpha = c_A(\mathbf{x}, t; [c_B^I = \gamma_B^I \neq 0]) \quad (2.4 - 1a)$$

and similarly a^I and α^I for c_A^I , b and β for c_B , and b^I and β^I for c_B^I , one has

$$\begin{aligned} c_A(\mathbf{x}, t) &= a(\mathbf{x}, t) + \alpha(\mathbf{x}, t) \\ c_A^I(\mathbf{x}, t) &= a^I(\mathbf{x}, t) + \alpha^I(\mathbf{x}, t) \\ c_B(\mathbf{x}, t) &= b(\mathbf{x}, t) + \beta(\mathbf{x}, t) \\ c_B^I(\mathbf{x}, t) &= b^I(\mathbf{x}, t) + \beta^I(\mathbf{x}, t) \end{aligned}$$

The advantage of this representation ("concentration field splitting") lies in the fact that the evolution of a , α etc., and of their statistical moments and correlations, is more easily predictable than of the reactant concentrations themselves.

One can use (2.4-1) and the ensemble averaged form of (1.3-3) to deduce relations between correlations of c_A , c_B and a , α , b , β , a^I , α^I , b^I and β^I (see Chapter 4). Thus, when the forward reaction in (1.3-1) dominates the backward (a situation which is expected to be valid in the near field of plume dispersion), and therefore $\langle c_A^I(\mathbf{x}, t) \rangle \geq \langle c_A(\mathbf{x}, t) \rangle$, $\langle c_B^I(\mathbf{x}, t) \rangle \geq \langle c_B(\mathbf{x}, t) \rangle$, it can be shown that

$$\langle c_A c_B \rangle = \langle \alpha \beta \rangle, \quad \langle c_A^I c_B^I \rangle = \langle \alpha^I \beta^I \rangle \quad (2.4 - 2)$$

and

$$\langle a(\mathbf{x}, t) \rangle = \langle a^I(\mathbf{x}, t) \rangle, \quad \langle b(\mathbf{x}, t) \rangle = \langle b^I(\mathbf{x}, t) \rangle \quad (2.4 - 3)$$

In this case, with the introduction of the *mixing functions*

$$M_{c_1 c_2} = \frac{\langle c_1 c_2 \rangle}{\langle c_1 \rangle \langle c_2 \rangle}, \quad M_{c_1^I c_2^I} = \frac{\langle c_1^I c_2^I \rangle}{\langle c_1^I \rangle \langle c_2^I \rangle} \quad (2.4 - 4)$$

one can obtain the expression:

$$\langle c_A c_B \rangle = \frac{\varphi}{\mu_A \mu_B} M_{AB}^I [\langle c_A \rangle - (1 - \mu_A) \langle c_A^I \rangle] [\langle c_B \rangle - (1 - \mu_B) \langle c_B^I \rangle] \quad (2.4 - 5)$$

where φ is the *reaction parameter* and μ_A, μ_B are the *mixing parameters* defined by

$$\varphi = \frac{M_{\alpha\beta}}{M_{\alpha\beta}^I} \quad (2.4-6)$$

and

$$\mu_A = \frac{\langle \alpha^I \rangle}{\langle c_A^I \rangle}, \quad \mu_B = \frac{\langle \beta^I \rangle}{\langle c_B^I \rangle} \quad (2.4-7)$$

In the special case of macroscopically uniformly mixed fields μ_A and μ_B represent the fractions of the total quantities of the fictitious inert surrogates of A and B that coexist in completely micromixed volumes.

Equation (2.4-5) is an exact relation. It expresses the unknown correlation in terms of mean values of the unknowns and in terms of parameters all of which except one, namely φ , depend only on inert scalar mixing. The problem of course has been transformed into the problem of estimation of these parameters.

A substantial simplification of (2.4-5) can be obtained in the case where $\langle c_B(\mathbf{x}, 0) \rangle$ is nonzero for all \mathbf{x} . This of course means that $\langle c_B^I(\mathbf{x}, t) \rangle$ is also nonzero for all \mathbf{x} and t and therefore $\langle a^I(\mathbf{x}, t) \rangle \equiv 0$, $\langle \alpha^I(\mathbf{x}, t) \rangle \equiv \langle c_A^I(\mathbf{x}, t) \rangle$, which give $\mu_A = 1$ for all (\mathbf{x}, t) (notice, however, that $\mu_B \neq 1$ in general). This result can be utilized for a typical atmospheric plume where the emissions of A (e.g. NO) have near source concentrations that are orders of magnitude higher than those of B (e.g. O₃). The fact $\langle c_A \rangle \gg \langle c_B \rangle$ near source implies that it will make no observable difference to the conversions of A if it were assumed that B is perfectly mixed with the emissions at the source, at a concentration equal to that of the ambient (in agreement with the idealization of the point source). Indeed, in such a case it does not make an appreciable difference to the overall evolution of reaction and the observed conversions of A if A and B are initially premixed or unpremixed. This further means that fine scale segregation of A and B inside the plume is induced mainly by the chemical reaction. This simplifies the analysis considerably, especially if it is assumed that the reaction is not infinitely fast and a local steady state with microscopic coexistence of

A and B prevails. It is then possible using intuitive arguments to suggest that

$$\mu_B \simeq \frac{1}{M_{AA}^I}, \text{ and } M_{AB}^I \simeq 1$$

are acceptable *closure assumptions*. It can further be shown, by examining the significance of the participating correlations under the aforementioned conditions, that φ should be of order one. This is corroborated by the analysis of Shu (1976), Lamb and Shu (1978), and Shu et al. (1978) for monodimensional systems.

Hence, to recapitulate, in the case of a point release of A into an initially uniform field of B , and under the assumption that the concentrations of A , at least near the plume axis, are much greater than the background concentration of B , we can approximate the term $\langle c_A c_B \rangle = \langle c_A \rangle \langle c_B \rangle + \langle c'_A c'_B \rangle$ by

$$\langle c_A c_B \rangle \simeq M_{AA}^I \langle c_A \rangle \langle c_B \rangle + (1 - M_{AA}^I) \langle c_B^I \rangle \langle c_A \rangle \quad (2.4 - 8)$$

where M_{AA}^I is a function characteristic of the state of *inert* species mixing in the plume.

Alternatively, if we consider the fluctuations $c_A^{I'}$ about $\langle c_A^I \rangle$, M_{AA}^I can be written as $M_{AA}^I = 1 + I_A^I$ where

$$I_A^I = \frac{(\sigma_A^I)^2}{\langle c_A^I \rangle^2} \text{ where } (\sigma_A^I)^2 = \langle (c_A^I)'^2 \rangle \quad (2.4 - 9)$$

is the relative intensity of concentration fluctuations of an inert emitted species in a plume, or "*intensity of stream segregation*" (see Chapter 4 for a more detailed discussion).

Introducing I_A^I we can write (2.4-8) as

$$\langle c_A c_B \rangle \simeq \langle c_A \rangle \langle c_B \rangle + I_A^I \langle c_A \rangle (\langle c_B^I \rangle - \langle c_B \rangle) \quad (2.4 - 10)$$

which of course is equivalent to

$$\langle c'_A c'_B \rangle \simeq I_A^I (\langle c_B^I \rangle - \langle c_B \rangle)$$

The overall mean rate of reaction (1.3-1) at a point will therefore be

$$\langle R \rangle \simeq \tilde{R} = k_f \langle c_A \rangle \langle c_B \rangle - k_f I_A^I \langle c_A \rangle (\langle c_B^I \rangle - \langle c_B \rangle) - k_b \langle c_P \rangle \quad (2.4-11)$$

Hence, all the effects of turbulence (or incomplete mixing) on the chemical kinetics have been incorporated in the second term of (2.4-11) which involves

- (i) the mean concentrations of the reactive species $\langle c_A \rangle$, $\langle c_B \rangle$ which are the actual unknown variables we want to estimate,
- (ii) the mean concentrations of inert surrogate species $\langle c_A^I \rangle$, $\langle c_B^I \rangle$, and
- (iii) the variance of fluctuations of an inert emitted species.

The form of the second term of (2.4-11) suggests that it can be interpreted as representing a *fictitious reverse reaction* that retards the overall kinetic scheme in comparison to perfectly mixed conditions. The kinetic constant $k_f I_A^I$ of this "reaction" will depend on position in the plume because I_A^I shows a strong dependence on axial and radial position. The "reactants" participating in this fictitious step are A and the portion of B at any point that has already undergone chemical reaction (and therefore it is not actually available at that point). Thus the term $\langle c_B^I \rangle - \langle c_B \rangle$ can be viewed as representing "occupied" or "de-activated" B molecules that participate in a backward reaction with A , with a kinetic constant that is determined by the intensity of turbulent fluctuations. The behavior of this term is determined by the relative magnitude of I_A^I , $\langle c_A \rangle$ and $(\langle c_B^I \rangle - \langle c_B \rangle)$.

Thus, the initial problem of solving the system of equations of type (1.3-6) with \mathcal{L}^M given by (1.3-7) has been reduced to solving

$$\mathcal{L}_K^M c_{A,B,P} = \tilde{r}_{A,B,C} \text{ with } \tilde{r}_A = \tilde{r}_B = -\tilde{r}_P = -\tilde{R} \quad (2.4-12)$$

where \tilde{R} is given by (2.4-11) and \mathcal{L}_K^M is given by (2.3-2).

2.5 THE WORKING COMPUTATIONAL SCHEME

2.5.1 Reduction of the Number of Equations:

The Local Phenomenal Extent of Reaction

When the number of independent reactions is smaller than the number of reacting species, stoichiometric relations can be combined with the concept of inert surrogate concentrations to reduce the number of partial differential equations needed to describe the evolution of multimolecular systems in turbulent, incompletely mixed, fields.

The conventional *extent* or *degree of advancement* of reaction is a useful tool in utilizing stoichiometric relations to simplify the kinetic description of chemical systems that evolve either in space or in time. For such systems the number of governing equations for the evolution of concentration fields can always be reduced to the number of independent reactions between the species. Then, at steady state, simple algebraic expressions relate the concentrations of all species to the extents of independent reactions. (Such a formulation is obviously useful when the number of reacting species is larger than the number of independent reactions). When however chemical reaction and macroscopic, as well as microscopic, dispersion effects are coupled and evolve *simultaneously in space and time*, the conventional formulations are no longer useful. For this reason we introduce here the concept of a local phenomenal extent for a spatially distributed reaction, which incorporates both stoichiometry and diffusion effects to simplify the description of a simultaneously reacting and diffusing mixture of species. Suppose the p species A_1, A_2, \dots, A_p participate in the reaction

$$0 = \sum_{i=1}^p \nu_i A_i$$

where $i = 1, 2, \dots, p$ and ν_i is the stoichiometric coefficient of species A_i , that takes place in an arbitrary flow field. In general the reactants will not be uniformly mixed

Thus, for the reaction $A + B \rightleftharpoons P$ we will have at any point \mathbf{x} $\langle c_A \rangle = \langle c_A^I \rangle - \langle \xi \rangle$, $\langle c_B \rangle = \langle c_B^I \rangle - \langle \xi \rangle$, and $\langle c_P \rangle = \langle c_P^I \rangle + \langle \xi \rangle$. Thus, instead of solving the system of equations (2.4-12) we need only solve one dynamic equation for $\langle \xi \rangle$:

$$\mathcal{L}_K^M \langle \xi \rangle = \tilde{R} \quad (2.5 - 3)$$

with \mathcal{L}_K^M given by (2.3-3).

The approximate reaction rate given by equation (2.4-11) can be written as a quadratic expression in $\langle \xi \rangle$, the coefficients being functions of properties of the inert surrogate fields:

$$\tilde{R} = \tilde{R}_1(\mathbf{x}, t) \langle \xi \rangle^2 + \tilde{R}_2(\mathbf{x}, t) \langle \xi \rangle + \tilde{R}_3(\mathbf{x}, t) \quad (2.5 - 4)$$

where

$$\begin{aligned} \tilde{R}_1 &= k_f(1 + I_A^I) \\ \tilde{R}_2 &= k_f \langle c_A^I \rangle (1 + I_A^I) + k_f \langle c_B^I \rangle + k_b \\ \tilde{R}_3 &= k_f \langle c_A^I \rangle \langle c_B^I \rangle - k_b \langle c_P^I \rangle \end{aligned} \quad (2.5 - 4a)$$

In situations relevant to atmospheric plumes, inert concentration fields can often be assumed to be described adequately by appropriate Gaussian formulas; in this case it is obvious that the computational burden involved in the solution of (2.4-12) is reduced significantly. Further, in cases of infinite rate chemistry, where pointwise equilibrium is assumed for the instantaneous concentrations and the mean rate is equal to zero, $\langle R \rangle = 0$ then only estimates for the inert surrogate concentration fields and the variance of inert species fluctuations are needed for the direct algebraic calculation of the reactive species concentration fields.

2.5.2 Estimation of Fixed Frame Concentrations

The mean location of the plume and the statistical properties of its meandering motion can be used to estimate reactive concentrations at any fixed point once the corresponding concentrations in the translating frame are calculated by the master module.

The problem is as follows: We seek the expected instantaneous concentration, $\langle \tilde{c} \rangle$ at the point $(\tilde{x}_1, \tilde{x}_2, \tilde{x}_3)$ of a fixed reference frame and let (x_1, b_2, b_3) be the fixed frame random coordinates (at time t) of the center of mass of a vertical plume cross-section passing through $x_1 \equiv \tilde{x}_1$. The instantaneous random concentration \tilde{c} at $(x_1, \tilde{x}_2, \tilde{x}_3)$ is of course exactly the concentration c of the moving frame measured at $(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3)$: $\tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \equiv c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3)$, and hence $\langle \tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \rangle \equiv \langle c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3) \rangle$. Now if $P_k(x_1; b_2, b_3) db_2 db_3$ represents the probability that the center of mass of the vertical plume cross-section at x_1 is in the area element (b_2, b_3) to $(b_2 + db_2, b_3 + db_3)$, then

$$\langle \tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \rangle = \int_{b_2} \int_{b_3} \langle c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3) \rangle P_k(x_1; b_2, b_3) db_2 db_3 \quad (2.5 - 5)$$

The probability density function $P_k(x_1; b_2, b_3)$ can be expressed in terms of the transition probability density for fluid particles in a turbulent field which is a quantity extensively studied in analyses of turbulent flows (Monin and Yaglom 1971, 1975; Hinze 1975; Seinfeld 1975). Typically $P_k(x_1; b_2, b_3)$ is assumed Gaussian,

$$P_k(x_1; b_2, b_3) = \frac{1}{2\pi\sigma_{M_2}\sigma_{M_3}} \exp\left(-\frac{b_2^2}{2\sigma_{M_2}^2}\right) \exp\left(-\frac{b_3^2}{2\sigma_{M_3}^2}\right) \quad (2.5 - 6)$$

where the σ_M 's are the standard deviations of meandering at x_1 . Then, relation (2.5-5) estimates $\langle \tilde{c} \rangle$ in a fixed frame through a convolution transform of the moving frame concentration $\langle c \rangle$, the transform having a Gaussian kernel (a Weierstrass transform – see Zemanian, 1968).

2.5.3 Summary of the Computational Scheme

To summarize the overall TRP Model, its equations, as applied to the problem $A(\text{plume species}) + B(\text{in ambient}) \rightleftharpoons P$, are given in Table 2-1 together with the parameters involved.

Numerical implementation of the scheme of Table 2-1 involves the following three-step sequence:

STEP 1: *Preprocessor settings - Peripheral Models Activation*

This initial step consists of selecting the appropriate method ("peripheral model") for calculating the inner level parameters to be utilized by the mixing-reaction equations (i.e. the relative dispersion parameters, the inert surrogate means and the plume intensity of stream segregation). The available options in the current version of the TRPM are discussed in Section 2.6.

STEP 2: *Master Module Calculations*

This step consists of the calculation of spatial reaction evolution in a meandering/rising frame of reference. In the model problem (three species - one independent reaction) the master module consists of the evolution equation for $\langle \xi \rangle$, a set of algebraic equations relating reactive species concentrations to $\langle \xi \rangle$, plus the calculations for the inert mixing problem, i.e. for the mean and the variance of the inert surrogate of the plume species.

The evolution of $\langle \xi \rangle$ is described by a reaction-diffusion equation, the chemical kinetics term being a second degree polynomial in ξ (equations (2.5-3), (2.5-4)). The coefficients of this polynomial are functions of position inside the plume and involve the aforementioned properties of the inert surrogate; these are calculated either from analytical expressions, when the inert dispersion problem allows for such solutions (e.g. Gaussian type formulas for the mean and the Localized Production of Fluctuations formulas) or from numerical solution of linear transport equations with apparent eddy diffusivities given by (2.3-1). An Alternating Direction Implicit finite difference scheme, that is appropriate for handling the nonlinearity of (2.5-3), is adopted for the grid solution of the equations for $\langle \xi \rangle$, $\langle c_A^I \rangle$ and $(\sigma_A^I)^2$ (see Appendix

Table 2-1

The TRPM Applied to the Model Problem $A + B \rightleftharpoons P$
 (Intrinsic Chemical Reaction Rate $R = k_f c_A c_B - k_b c_P$)

A. GOVERNING EQUATIONS FOR TURBULENT MIXING AND REACTION: MASTER MODULE

- (i) *Dynamic Evolution Equations (for steady release of A in ambient B)*
 (ia) *Auxiliary Calculations*

$$\mathcal{L}_K^M \langle c_A^I \rangle = 0; \langle c_A^I \rangle = S\delta(\mathbf{x}) \text{ at } \mathbf{x} = 0, \langle c_A^I \rangle \rightarrow 0 \text{ at } x_2 \rightarrow \pm\infty, x_3 \rightarrow \infty, \frac{\partial \langle c_A^I \rangle}{\partial x_3} = 0 \text{ at } x_3 = -h_T$$

$$\langle c_B^I \rangle = \langle c_B \rangle^0, \langle c_P^I \rangle = \langle c_P \rangle^0$$

$$\mathcal{L}_K^M (\sigma_A^I)^2 = 2K_i \left(\frac{\partial \langle c_A^I \rangle}{\partial x_i} \right)^2 - \frac{(\sigma_A^I)^2}{kt}; (\sigma_A^I)^2 = 0 \text{ at } \mathbf{x} = 0, (\sigma_A^I)^2 \rightarrow 0 \text{ at } x_2 \rightarrow \pm\infty, x_3 \rightarrow \infty, (\sigma_A^I)^2 = 0 \text{ at } x_3 = -h$$

- (ib) *Local Phenomenal Extent of Reaction Calculations*

$$\mathcal{L}_K^M \langle \xi \rangle = R_1(\mathbf{x}) \langle \xi \rangle^2 + R_2(\mathbf{x}) \langle \xi \rangle + R_3(\mathbf{x}); \langle \xi \rangle = 0 \text{ at } \mathbf{x} = 0, \langle \xi \rangle \rightarrow 0 \text{ at } x_2 \rightarrow \pm\infty, x_3 \rightarrow \infty, \frac{\partial \langle \xi \rangle}{\partial x_3} = 0 \text{ at } x_3 = -h_T$$

where

$$\mathcal{L}_K^M \langle \cdot \rangle = -\bar{u}_1 \frac{\partial \langle \cdot \rangle}{\partial x_1} + K_{R_2} \frac{\partial^2 \langle \cdot \rangle}{\partial x_2^2} + K_{R_3} \frac{\partial^2 \langle \cdot \rangle}{\partial x_3^2}, K_{R_i} = \frac{\bar{u}_1}{2} \frac{d\sigma_{R_i}^2}{dx_1}$$

and

$$\bar{R}_1(\mathbf{x}) = k_f(1 + I_A^I); \bar{R}_2(\mathbf{x}) = k_f[\langle c_A^I \rangle(1 + I_A^I) + \langle c_B^I \rangle] + k_b; \bar{R}_3(\mathbf{x}) = k_f \langle c_A^I \rangle \langle c_B^I \rangle - k_b \langle c_P^I \rangle$$

$$I_A^I = \frac{(\sigma_A^I)^2}{\langle c_A^I \rangle^2} \text{ with } (\sigma_A^I)^2 = \langle (c_A^I)^2 \rangle$$

- (ii) *Local Stoichiometry at \mathbf{x}*

$$\langle c_A \rangle = \langle c_A^I \rangle - \langle \xi \rangle, \langle c_B \rangle = \langle c_B^I \rangle - \langle \xi \rangle, \langle c_P \rangle = \langle c_P^I \rangle + \langle \xi \rangle$$

B. ESTIMATION OF FIXED FRAME CONCENTRATIONS: COMPLEMENTARY MODULE

- (i) *Plume Rise Effects*

Plume Rise Model gives $\langle b_3 \rangle = \langle b_3(x_1) \rangle$

(Alternatives: (i) Brigg's formulas, (ii) Schatzmann's integral scheme)

- (ii) *Meandering Effects*

$$\langle \bar{c}(x_1, \bar{x}_2, \bar{x}_3) \rangle = \int_{b_2} \int_{b_3} \langle c(x_1, \bar{x}_2 - b_2, \bar{x}_3 - b_3) \rangle P_k(x_1; b_2, b_3) db_2 db_3$$

$$P_k(x_1; b_2, b_3) = \frac{1}{2\pi\sigma_{M_2}\sigma_{M_3}} \exp\left(-\frac{b_2^2}{2\sigma_{M_2}^2}\right) \exp\left(-\frac{b_3^2}{2\sigma_{M_3}^2}\right)$$

Notation: A in-plume species; B ambient species; $\langle c_i^I \rangle$ mean inert surrogate concentration; $\langle c_i \rangle^0$ mean ambient concentration; c_i' instantaneous fluctuation about the mean value; k_f and k_b forward and backward reaction rate constants; ξ local phenomenal extent of reaction; $(\sigma_A^I)^2$ and I_A^I variance and intensity of segregation for the inert surrogate of A. \bar{x}_i fixed frame coordinates; x_i meandering frame coordinates; b_i coordinates of instantaneous centerline; σ_i , σ_{R_i} and σ_{M_i} : absolute dispersion, relative dispersion and meandering parameters; \bar{u}_1 mean wind field along the plume centerline; P_k Gaussian fluid particle position pdf; h_T effective source height.

A3.1). In the case analytical expressions are used for $\langle c_A^I \rangle$ and $(\sigma_A^I)^2$, one can avoid the grid solution and obtain an estimate of $\langle \xi \rangle$ at any arbitrary point of the field by direct transformation of (2.5-3) into integral form and application of an iterative method (see Chapter 3, Section 3.3.3).

STEP 3: *Post-Processing Calculations*

In this final step, expected (or time averaged) reactive species concentrations at points fixed relative to the ground are estimated. More specifically, this step consists of:

3A. Selecting the outer level parameters, i.e.,

- (i) specifying the plume rise model to be used for determining the mean plume path, and
- (ii) estimating the meandering parameters.

(The available options are discussed in the next section).

3B. Calculating fixed frame concentrations via the convolution relation (2.5-5).

Further calculations such as estimation of spatial (e.g., crosswind plane) average concentrations can also be readily performed simultaneously with Step 3.

2.6 DETERMINATION OF PARAMETERS IN THE REACTIVE PLUME MODEL

In this section we summarize basic information regarding the parameters that are needed in the TRPM for quick reference and in order to provide an overview of the entire computational procedure (and the possible alternative choices in this procedure) that must be followed for an application of the model. A more detailed exposition can be found in Chapters 5, 6 and 7.

2.6.1 Inner Level Parameters

(a) Relative Dispersion Parameters

(See also Chapter 6)

Methods providing estimates of relative or two-particle dispersion parameters can be classified as:

- (i) Similarity theory combined with empirical information from field and laboratory measurements of puffs or instantaneous plume realizations (Plate, 1982; Hanna et al., 1982; Hanna, 1984).
- (ii) Analytical and numerical Lagrangian studies of fluid particle motion based on Langevin equations (Gifford, 1982; Durbin, 1980; Sawford, 1982; Lee and Stone, 1983ab).
- (iii) Fluid particle transition probability density methods (Leslie, 1973-Sections 8.6 and 12.2; Lundgren, 1981; Jiang, 1985).
- (iv) Spectral methods - An analysis of the motion of fluid particle pairs shows that the relative dispersion parameters cannot be expressed directly in terms of velocity spectra because the correlation of relative fluid particle velocities is not stationary (*). Indirect techniques, based on appropriate filtering of spectral functions were originated by Smith and Hay (1961). More recent attempts to obtain information on

(*) The two-particle dispersion counterpart of Taylor's formula will involve weighted integrals of the temporal correlation of the relative two-particle acceleration (Lin and Reid, 1963).

inated by Smith and Hay (1961). More recent attempts to obtain information on relative dispersion and meandering through a direct single-step filtering of measured one-dimensional Eulerian velocity spectra have produced contradictory results (Sheih, 1980; Rowe, 1981; Mikkelsen and Troen, 1981).

We will adopt the following two options for relative dispersion parameters:

- (1) Use of simple similarity or empirical relations (Csanady, 1973; Hanna, 1984) in power law form.
- (2) Use of an iterative filtering algorithm to deduce information from observed velocity spectra. This algorithm is briefly described in the next paragraph; for further discussion see Chapter 6.

Atmospheric field measurements during the last two decades have resulted in reliable universal forms of Eulerian velocity spectra (see, e.g., Caughey, 1982; Panofsky and Dutton, 1984-pp174-228). Given the Eulerian velocity spectral density in the i -th direction $S_{ii}^E(n)$ (normalized), and the corresponding velocity variance $[u_i'^2]_{\infty,0}$ where the subscripts $\infty, 0$ denote sampling of instantaneous values over an infinite sampling time, and utilizing the Hay-Pasquill (1959) hypothesis for the relation among Eulerian and Lagrangian quantities, one obtains the following relation for the absolute dispersion parameters,

$$\sigma_i^2 = [u_i'^2]_{\infty,0} t^2 \int_0^\infty S_{ii}^E(n) \frac{\sin^2 \pi n(t/\beta)}{(\pi n(t/\beta))^2} dn \quad (2.6 - 1)$$

where $\beta = a\bar{u}_1 [u_i'^2]_{\infty,0}^{-1/2}$, with $a \simeq 0.4$ to 0.6 . Then, using a low frequency filter we obtain a first estimate of the relative dispersion parameter through

$$\sigma_{Ri}^2 = [u_i'^2]_{\infty,0} t^2 \int_0^\infty S_{ii}^E(n) \frac{\sin^2 \pi n(t/\beta)}{(\pi n(t/\beta))^2} \left[1 - \frac{\sin^2 \pi n\tau}{(\pi n\tau)^2} \right] dn \quad (2.6 - 2)$$

where the averaging time τ is taken equal to

$$\tau = \frac{2\sqrt{2}\sigma_i}{\bar{u}_1} \quad (2.6 - 3)$$

Then we refine the estimate of σ_{R_i} by replacing σ_i in the expression for τ with the estimate of σ_{R_i} . This procedure is repeated until convergence is achieved.

The spectral functions of Kaimal (1973) and Hojstrup (1982) for stable and neutral-unstable conditions, respectively, can be adopted for use with this approach.

*(b) Inert Surrogate Means
and the Intensity of Segregation
(See also Chapter 5)*

The chemical closure scheme for point source plume-unpremixed reactants involves mean concentrations of inert surrogates and the fine scale intensity of stream segregation for the instantaneous plume. In the present work the latter quantity was defined as the ratio of the variance to the square of the mean concentration of an inert surrogate of the emitted reactant, at every point inside the instantaneous plume boundaries. Thus estimates for the first two moments of the instantaneous concentration field are needed.

Calculation of mean concentrations is, of course, a widely studied problem in atmospheric diffusion theory. At the present level of development of the TRPM the two alternatives of using Gaussian type analytical expressions or solving $\mathcal{L}_K^M \langle c_A^I \rangle = 0$ numerically are available.

The variance $(\sigma_A^I)^2$ of c_A^I is also calculated either

- (i) from the analytical expressions provided by the Localized Production of Fluctuations Model (which is presented in detail in Chapter 5), when a Gaussian formula offers an adequate description of the mean instantaneous field, or
- (ii) from numerical solution of the $(\sigma_A^I)^2$ -transport equation:

$$\mathcal{L}_K^M (\sigma_A^I)^2 = 2K_i \left(\frac{\partial \langle c_A^I \rangle}{\partial x_i} \right)^2 - \frac{(\sigma_A^I)^2}{kt} \quad (2.6-4)$$

(summation convention implied), with k a constant in the range $1/3$ to $3/2$, subject to boundary conditions requiring that $(\sigma_A^I)^2$ vanishes at the ground surface.

that may be appropriate for use with the TRPM under special conditions, are also discussed in Chapter 5 and its appendices.

2.6.2 Outer Level Parameters

(a) Mean Plume Path (Plume Rise)

(See also Chapter 7)

Determining the path and expansion of an actual plume in the near-source region requires analyzing the problem of the merging of two turbulent flows, i.e., of the emissions flow, possibly associated with significant momentum and buoyancy fluxes, and of the ambient, density stratified turbulent atmospheric flow, up to that point in time where the properties of the ambient completely dominate the system (Briggs, 1975, 1984; List, 1982; Gebhard et al., 1984).

For use with the TRPM two alternatives are provided:

- (1) Use of Briggs' (1975) formulas that are the most widely accepted in applications (Hanna et al., 1982). These formulas result from a combination of field observations, dimensional analysis, and simple entrainment hypotheses.
- (2) Use of a two- or three-dimensional version of Schatzmann's (1978, 1979) integral model that is formulated for arbitrary temperature and density differences inside the plume and for arbitrary stratification (Appendix A7.2).

(b) Meandering Parameters

(See also Chapter 6)

Meandering parameters σ_{M_i} are determined through

$$\sigma_{M_i}^2 = \sigma_i^2 - \sigma_{R_i}^2$$

Other processes that may contribute to the total variance, such as shear and buoyancy are assumed negligible here; in a more detailed calculation, one can use estimates of the contribution to the variance of these processes as reported, e.g., in Csanady (1973) and Pasquill (1974, 1975). The σ_{R_i} 's are calculated as described in Subsection 2.6.1; a variety of possible alternatives is available in the literature for the σ_i 's (see,

e.g., Hanna et al., 1982; Seinfeld, 1983, for recent reviews). The "best" estimate for use must be chosen on the basis of the information that is relevant to the particular application. If velocity spectra are available, then the spectral forms of Taylor's formula (equation (2.6-1)) offer a procedure that relies on theory and utilizes a rich source of information on atmospheric turbulence, i.e., its spectral density.

2.7 CONCLUSIONS

A modular scheme for describing reaction evolution in plumes has been developed, focusing on the construction of a method that accounts for the effects of mixing on bimolecular reactions between constituents of the plume and the background air.

A major advantage of the present approach is that all fine scale mixing effects are incorporated in the chemical kinetic terms and that the transport part of the governing equations has to account only for macromixing. Consequently, even if the bimolecular reaction under consideration is coupled with a network of other physical or chemical processes involving the participating species, only terms corresponding to the above reaction will have to be modified via the adopted chemical closure scheme. Another important point is that, because of the "decoupling of mixing and reaction" character of the closure scheme, even if more than one independent bimolecular reactions between unpremixed reactants occurs in the system, the parameters of the chemical closure, involving inert surrogate properties, will have to be estimated only once. Further, the equations governing these parameters are not coupled with the equations for the reaction progress variables. In conclusion, the TRPM provides a flexible scheme appropriate for assessing the effects of incomplete mixing on nonlinear atmospheric reactions. The "core" of the model, contained in the master module, is relatively simple - considering the variety of phenomena it addresses. Indeed, the chemical closure approximation does not require further evolution equations for high order concentration correlations; instead, it requires parameters that can all, optionally, be expressed by closed analytical formulas and provides a direct substitute of the correlation of fluctuation in the mean kinetic term. Further, the concept of the local phenomenal extent of reaction improves the computational efficiency of the model, also providing a means for describing the local level of the interaction between dispersive and reactive phenomena.

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CHAPTER 3

THE TURBULENT REACTING PLUME MODEL (TRPM): APPLICATION TO THE NO - NO₂ - O₃ SYSTEM

3.1 INTRODUCTION

In this chapter we present a first evaluation of the Turbulent Reacting Plume Model (TRPM) that was described in Chapter 2. The reaction considered is that between NO, emitted from a point source, and ambient O₃. This particular system of reactants was chosen because (see also Chapter 1):

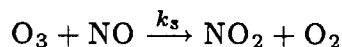
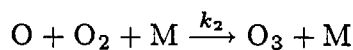
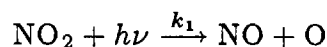
- (i) it is typically the most important system in the near field dispersion phase of plumes from large combustion sources (McRae et al., 1982; Burton et al., 1983),
- (ii) its kinetics are characterized by time scales that are of comparable magnitude to those of the atmospheric mixing processes and, consequently, its evolution is determined by a strong and complex coupling of reaction and dispersion phenomena, and
- (iii) there are available detailed data bases that show explicitly the effects of the aforementioned coupling as well as the inability of simple formulations to describe it.

A set of laboratory data is chosen to compare with TRPM predictions for the effects of incomplete macro- and micro- mixing on nonlinear chemistry. The controlled conditions to which these data are relevant, and the relatively ample amount of information regarding the characteristics of the flow and the dispersion process, allow for quantitative conclusions and avoid the uncertainties associated with complex field

flows and, necessarily, incomplete or limited measurements. The simple geometrical characteristics of the experimental flow under study, combined with the modular formulation of the TRPM, lead to the construction of a rather simple computational scheme that provides a direct testing of the "master module" of the TRPM.

3.2 ATMOSPHERIC MIXING AND THE O₃ - NO - NO₂ SYSTEM

The three principal reaction steps involved in the O₃-NO-NO₂ photolytic cycle are (*)



The value of k_1 depends on light intensity and it varies between 0 and 0.6 min⁻¹ for typical sunlight intensities. The values of k_2 and k_3 are obtained from the following relations (Hampson and Garvin, 1978) at 1 atm pressure with T in degrees K:

$$k_2 = \frac{0.246}{T^2} \exp\left(\frac{510}{T}\right) \text{ ppm}^{-2} \text{ min}^{-1}$$

$$k_3 = \frac{9.2 \times 10^5}{T} \exp\left(\frac{-1450}{T}\right) \text{ ppm}^{-1} \text{ min}^{-1}$$

Under most commonly encountered conditions the above reactions proceed at a rate nearly two orders of magnitude faster than any of the other steps in photochemical smog formation that involve ozone (Stedman and Jackson, 1975). Since the combustion products from large point sources are rich in nitrogen oxides and typically have low concentrations of reactive hydrocarbons (McRae et al., 1982), the near source plume chemistry is dominated by the above O₃-NO_x cycle. Thus there arises the need for estimating the fraction of nitric oxide (NO) that is converted to nitrogen dioxide (NO₂) during the initial phase of plume dispersion, before the plume has

(*) An additional source of nitrogen dioxide in plumes is the thermal oxidation of nitric oxide by oxygen. This process is only significant for very high nitric oxide concentrations and is usually omitted in photochemical reaction mechanisms or just used to correct the source concentration ratio of nitrogen oxides; an exposition of the latter approach, based on McRae et al., (1982), is given in Appendix A3.2.

grown to the size of a typical computational cell of an airshed model. After that point a complete reaction mechanism considering hydrocarbon and radical interactions will have to be employed.

The main oxidizing reaction $O_3 + NO \rightarrow NO_2 + O_2$ for typical atmospheric concentrations would have a half life of approximately 30 seconds for well mixed volumes. Under such conditions many investigators have made the assumption that the ozone production and decay rates are in equilibrium and derived the photostationary state approximation, PSSA, (Leighton, 1961)

$$k_3 c_{NO} c_{O_3} = k_1 c_{NO_2} \quad (3.2 - 1)$$

This relation will hold locally for systems that are mixed at the molecular level (e.g., smog chambers). One however will not be able to substitute in this equation temporally or spatially averaged concentrations \bar{c}_{NO} , \bar{c}_{NO_2} , \bar{c}_{O_3} obtained from real atmospheric situations where the mixing of pollutants with air is not complete (Seinfeld, 1977; Bilger, 1978). This fact (which is also true for ensemble means of concentrations) is due to the macroscopic and microscopic inhomogeneities of real concentration fields. Thus, ensemble averaging of (3.2-1), where k_1 , k_3 are assumed non-random, (*) does not lead to a relation of the form $k_3 \langle c_{NO} \rangle \langle c_{O_3} \rangle = k_1 \langle c_{NO_2} \rangle$ but to

$$k_3 \langle c_{NO} \rangle \langle c_{O_3} \rangle + k_3 \langle c'_{NO} c'_{O_3} \rangle = k_1 \langle c_{NO_2} \rangle \quad (3.2 - 2)$$

The parameters usually employed to depict the invalidity of relation (3.2-1) for averaged concentrations are the so-called photostationary state parameter (PSSP) λ , defined in terms of averaged concentrations (see e.g., Bilger, 1978):

$$\lambda = \frac{k_3 \langle c_{O_3} \rangle \langle c_{NO} \rangle}{k_1 \langle c_{NO_2} \rangle} \quad (3.2 - 3)$$

(*) Actually random fluctuations in light intensity and, to a lesser degree, in temperature cause inevitable variations of the rate constants. One can incorporate this variation in the kinetic equations by decomposing the rate coefficients into mean and fluctuating components: (see, e.g. Kewley, 1978, and Appendix A3.3

and the photostationary state number (see e.g., Stedman and Jackson, 1975) which is simply the inverse of λ . From (3.2-2) one obtains

$$\lambda = \frac{1 - k_3 \langle c'_{O_3} c'_{NO} \rangle}{k_1 \langle c_{NO_2} \rangle} \quad (3.2-4)$$

Deviations of λ from unity (which is the value it would assume if defined in terms of instantaneous random concentrations) depend on the sign and magnitude of the correlation $\langle c'_{O_3} c'_{NO} \rangle$. For the initial stages of plume dispersion (in general for the admixing of fresh emissions) we expect the correlation to be negative and hence λ to be greater than unity. For smoggy air mixing with clean air one can expect a positive correlation and therefore λ less than unity. (If one also considers fluctuations in light intensity—which affect k_1 —one would expect a negative correlation of these fluctuations with c_{NO_2} and therefore a reducing effect on the value of λ .)

Measurements in polluted atmospheres have produced values of λ ranging from 0.3 to 7.5. Eschenroeder and Martinez (1972), from measurements in Los Angeles, report values of λ less than unity (down to 0.3) at low ambient ozone concentrations. These values increase drastically with increased mean ozone concentrations (e.g., they report values of λ greater than 7 for ozone concentrations in the range of 24 pphm). Stedman and Jackson (1975) report on values of $1/\lambda$ from measurements of ambient air quality in Detroit. Using 400 data sets they found that $1/\lambda$ was equal to 1.01 with a standard deviation of 0.2 and a standard error of the mean equal to 0.01. Other experimental results obtained during the Sydney Oxidant Study (Kewley and Post, 1978) also show variations of λ both above and below unity. Theoretical analyses of the problem in terms of simple descriptions of the state of incomplete mixing in the atmosphere have been presented by Calvert (1976), Seinfeld (1977), Bilger (1978), Kewley (1978, 1980), Kewley and Bilger (1979); formulations relevant to these analyses are also incorporated in some of the existing reactive plume models.

During the night reaction $NO_2 \rightarrow NO + O$ does not take place and the evolution of the system is determined by reaction $O_3 + NO \rightarrow NO_2 + O_2$. No photostationary state approximation can be invoked in this case but of course the conversion of NO

to NO_2 is still retarded by the mixing processes. With respect to modeling, the absence of a "reference" equilibrium state, that provides a first approximation to the solution of the problem, in general makes the case of the irreversible system described by $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ more difficult to handle (unless an "infinitely fast rate" assumption is invoked).

Various sets of field data relevant to nitrogen oxides-ozone chemistry in point source plumes are available (see, e.g., Burton et al., 1983, for a list and discussion of various field studies), the most widely referenced probably being those of Davis et al. (1974) and Hegg et al. (1977). However, incomplete information regarding the complex flow field and various aspects of the dispersion process, variations in temperature and light intensity, the possibility of changing source conditions, and the presence of hydrocarbons in the atmosphere, prohibit the quantitative association of observed effects with the fundamental underlying processes. Consequently, comparison of field data with theoretical calculations is presently meaningful only in a qualitative manner; proper initial testing and validation of a reacting plume model requires comparison with well controlled laboratory data where the uncertainty of "side effects" is kept to a minimum.

Laboratory studies of the reaction between nonpremixed O_3 and NO have been conducted by Shea (1977) for a turbulent O_3 jet in a NO environment, by Builtjes (1981, 1983) for a nonbuoyant NO plume in an O_3 environment, in a wind tunnel simulating a neutral atmospheric boundary layer, and by Komori and Ueda (1984) for a NO jet into a nonturbulent coflowing stream containing O_3 and for a NO plume into a grid-generated turbulent stream.

The set of data most appropriate for testing the capability of the TRPM to calculate the effect of mixing on plume chemistry, under conditions relevant to atmospheric flows, seems to be provided by the experiments of Builtjes and is briefly discussed in the next section, in relevance to the needs of the present work.

3.3 THE EXPERIMENTAL DATA BASIS AND THE TRPM EQUATIONS

3.3.1 The Nature of the Experimental Data

The experimental data basis provided by the work of Builtjes (1981, 1983) consists of averages over sets (to be seen as statistical samples from the perspective of this work) of short term point measurements of NO, NO_x and O₃ concentrations, for an elevated, non-buoyant, "point" source plume in a wind tunnel. The wind tunnel (with a test section 10 m long and a cross-section of $2.65 \times 1.2 \text{ m}^2$) simulated a neutral atmospheric boundary layer above grassland at a scale 1:500. The respective ratio of time scales of processes in the wind tunnel and in the atmosphere was estimated to be approximately 1:35. Details of the atmospheric boundary layer simulation can be found in Builtjes and Vermeulen (1980). The details of the reacting plume experiments are given in Builtjes (1981) and are further discussed in Builtjes (1983); the essential parameters of these experiments are given here in Table 3-1.

The source NO_x was entirely in the form of NO, a constant mean background concentration of O₃ was maintained, and the experiments were performed "in the dark"; no measurable quantities of hydrocarbons were present in the wind tunnel. Thus reaction $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ was governing the system as the sole producer of NO₂. Transverse (horizontal) concentration profiles of NO, NO_x and O₃ were measured at the height of the source at various distances downwind. At each point of these transverse profiles, and for each experiment, the statistical sample of measurements contains ten 30-second averaged O₃ values together (a) with five 1-minute averaged NO_x values, and, (b) with five 1-minute averaged NO values, as well as five 30-second averaged O₃ values without the NO plume present. These data were averaged, leading to one O₃, NO_x, NO and NO₂ = NO_x-NO concentration value at that point. The reproducibility of the measurements was approximately 15 % for O₃, 25 % for

Table 3-1
Parameters for the Wind Tunnel Experiment
(Bultjes, 1981, 1983)

NO Source Data

$$S \text{ (pure } NO) = 0.0110 \text{ m}^3 \text{ s}^{-1}$$

$$\bar{c}_{NO} \text{ at } z = 0 = 3900 \text{ ppm}$$

$$\text{source height } h = 0.14 \text{ m}$$

$$\text{source exit velocity } u_e = 0.4 \text{ m s}^{-1}$$

$$\text{source diameter} = 0.003 \text{ m}$$

Ambient Data

$$\text{ambient ozone concentration } \bar{c}_{O_3}^{\text{av}} = 0.350 \text{ ppm}$$

$$\text{integral length scale (at } z = h) = 0.3 \text{ m}$$

$$\text{average turbulence intensity (at } z = h) = 0.1$$

$$\text{mean wind velocity (at } z = h) = 0.4 \text{ m s}^{-1}$$

$$\text{boundary layer thickness} = 0.8 \text{ m}$$

$$\text{(Typical Temperature Range: } 16^\circ\text{C} - 20^\circ\text{C)}$$

NO_x and 30 % for NO, with a subsequent very large scatter in the estimated NO_2 values. (The reproducibility was in general better along and close to the centerline). These facts suggest that the O_3 sample averages should be better approximations of theoretical ensemble means of instantaneous values than the corresponding averages of NO and NO_x . Subsequent comparisons with TRPM calculations will therefore focus mainly on O_3 values.

In addition to the measurements of concentrations and ambient flow properties the experimental data base contains some direct information regarding the dispersion process. This information will be used as "validated input" in the calculations, reducing the uncertainty associated with dispersion related parameters and allowing to focus on the testing of the master module of the TRPM.

3.3.2 Parameters for the TRPM Calculations

(a) Dispersion Parameters

and Mean Surrogate Concentrations

The wind-tunnel plume showed only insignificant meandering. Thus in the following the plume envelope is assumed practically indistinguishable from the *expected* boundaries of the instantaneous plume. The dispersion parameter in the y (transverse horizontal) direction for the inert plume was estimated from measurements (of SF_6 , of NO in an O_3 -free environment and of total NO_x in an environment containing O_3) as $\sigma_y = 0.072x^{0.907}$ where x is the downwind distance from the source (x and σ_y in meters). Data related to the distribution of concentrations in the vertical (z) direction are not available; in the absence of other relevant information it was assumed that $\sigma_z = 1/2\sigma_y$, which is a classic choice in the case of neutral boundary layers (Csanady, 1973 - Section 3.12). The values of concentrations along the centerline (for all the aforementioned releases) exhibit good agreement with Gaussian plume calculations for these values of the dispersion parameters σ_y and σ_z . Figure 3-1 contains the centerline calculations together with the measured values of total NO_x in the reactive plume experiments.

Direct comparison of predictions with observed transverse profiles is difficult because of the inherent randomness of the concentration data. Figure 3-2a shows crosswind values of total NO_x (non-dimensionalized with the associated theoretical centerline concentration), measured horizontally at source height at various distances downwind, in comparison with the corresponding Gaussian estimates, versus the dimensionless distance y/σ_y from the centerline. Each depicted experimental value in this figure is the average of five short term measurements at a point, as mentioned earlier; different values at approximately the same y/σ_y correspond to measurements at different downwind positions. (It is obvious from the existing scatter in the data that averages over five values are very poor approximations to ensemble means.) When however one averages the different data corresponding to the same y/σ_y , thus improving the approximation of the relevant ensemble mean value, one discovers a satisfactory agreement between measurements and calculations, as shown in Figure 3-2b. (Actually averages were taken over data in the intervals 0 to $0.2y/\sigma_y$, $0.2y/\sigma_y$ to $0.4y/\sigma_y$, etc., since the dimensionless positions of the measurements at different downwind distances were not usually identical). It can therefore be claimed that the Gaussian plume equation

$$\langle c_{\text{NO}_x} \rangle = \frac{S}{2\pi\sigma_y\sigma_z\bar{u}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left\{ \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \right\} \quad (3.3-1)$$

with the source located at $(x, y, z) = (0, 0, h)$, is a valid model for the expected concentrations of the inert surrogate of NO (which in the present case is identical to total NO_x).

(b) *The Intensity of Segregation*

The second auxilliary calculation, besides that of the mean $\langle c_{\text{NO}_x} \rangle$, required by the master module of the TRPM, is that of the variance σ_c^2 of instantaneous total NO_x concentrations. (The intensity of stream segregation, involving these two quantities, participates in the turbulent kinetics expression of the TRPM). Since a

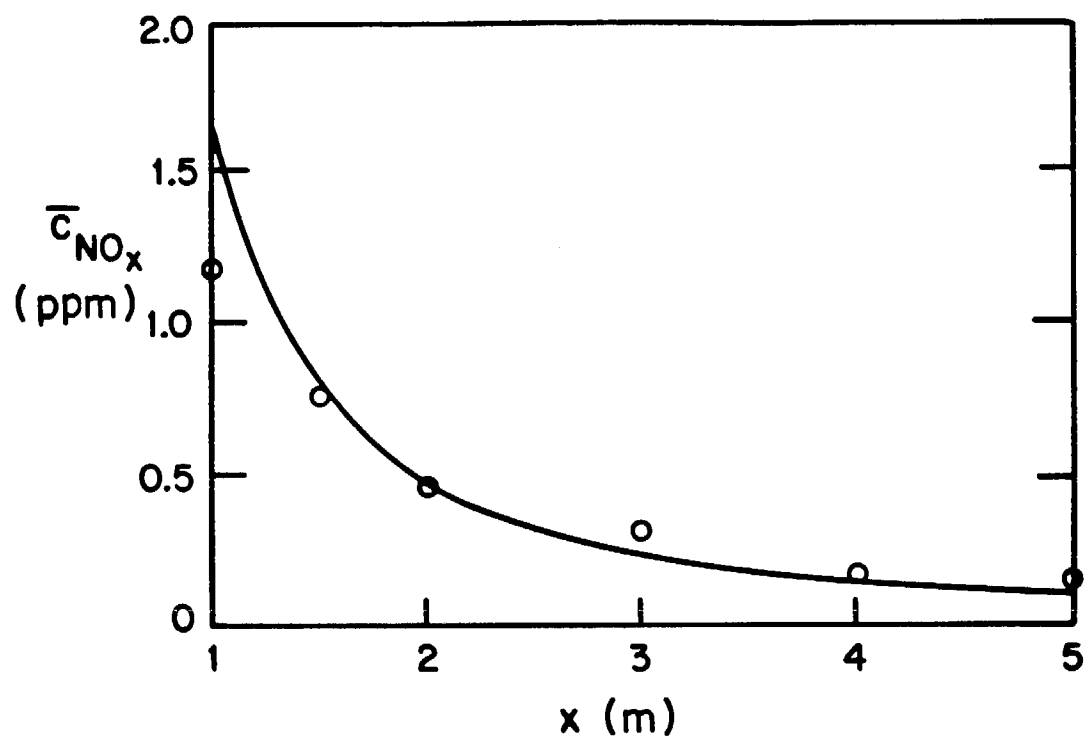


Figure 3-1

Total NO_x Concentrations along the Plume Centerline:
Data of Builtjes (1981) and Gaussian Plume Calculations.

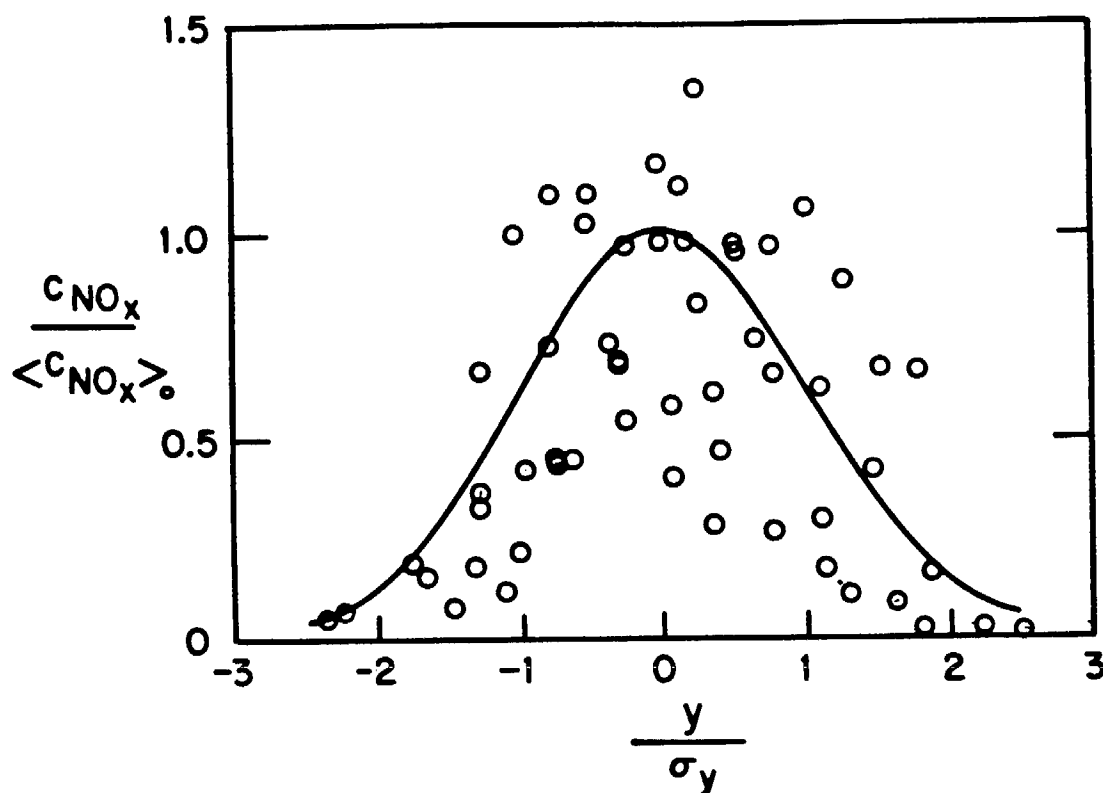


Figure 3-2a

Total NO_x Concentrations

Horizontally at Source Height and at Various Downwind Distances (1 to 5 m):

Data of Builtjes (1981) and Gaussian Plume Calculations

(both normalized with respect to the theoretical centerline value)

vs the Dimensionless Crosswind Distance y/σ_y from the Plume Centerline.

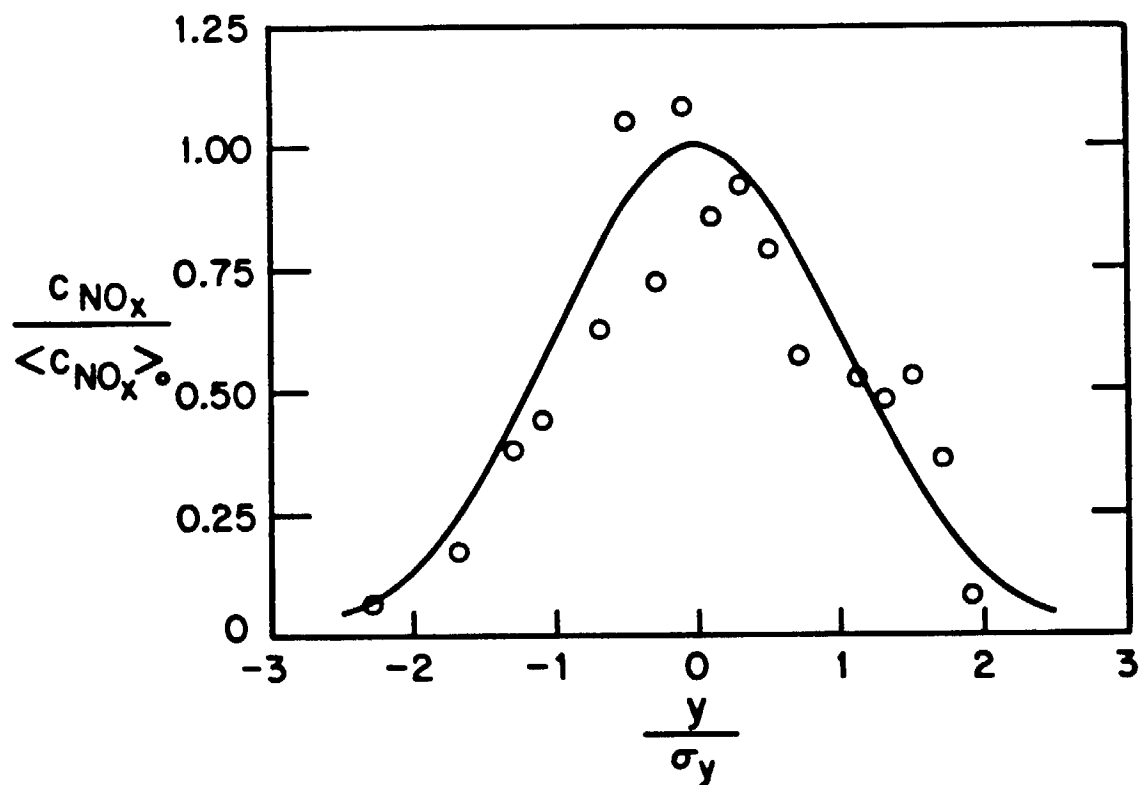


Figure 3-2b

Total NO_x Concentrations as in Figure 3-2a,
with the Experimental Values Replaced by the Averages of Measurements
(corresponding approximately to the same y/σ_y)
(See text for details)

Gaussian formula is assumed to provide an adequate description of the mean of the “instantaneous” NO_x field in the present case, we adopt the Localized Production of Fluctuations Model for σ_c^2 (Chapter 5):

$$\begin{aligned} \sigma_c^2(x, y, z) = & \left(\frac{S}{2\pi u} \right)^2 \frac{p \omega^{A_1-1}}{\sigma_y(\zeta) \sigma_z(\zeta) \sigma_y(x-\zeta) \sigma_z(x-\zeta)} \exp \left(-\frac{y^2}{2\sigma_y^2(x-\zeta)} \right) \times \\ & \times \exp \left(-\frac{ab}{2\sigma_y(x-\zeta) \sigma_z(x-\zeta)} \right) \left[\exp \left(-\frac{(z-h)^2}{2\sigma_z^2(x-\zeta)} \right) I_0 \left(\frac{\sqrt{a^2(z-h)^2 + b^2 y^2}}{\sigma_y(x-\zeta) \sigma_z(x-\zeta)} \right) \right. \\ & \left. - \alpha \exp \left(-\frac{(z+h)^2}{2\sigma_z^2(x-\zeta)} \right) I_0 \left(\frac{\sqrt{a^2(z+h)^2 + b^2 y^2}}{\sigma_y(x-\zeta) \sigma_z(x-\zeta)} \right) \right] \end{aligned} \quad (3.3-2)$$

where I_0 is the modified Bessel function of order zero, ω is the dimensionless localization parameter (between 0 and 1), $\zeta = \omega x$, p is the exponent in the power law for σ_y , σ_z (i.e. $p = 0.907$ here), $a = 3/4\sqrt{\pi}\sigma_y(\zeta)$, $b = 3/4\sqrt{\pi}\sigma_z(\zeta)$, and A_1 is a constant factor (between 1.5 and 3.0) relating the fluctuations dissipation time scale to the dispersion time. The parameter α equals unity for a “perfectly absorbing boundary”, i.e. for $\sigma_c^2 = 0$ at the ground surface, and would be zero in the absence of ground effects.

Measurements in the reacting plume experiments show that the centerline intensity of segregation $I_g^c = I_s(x, 0, 0)$, where $I_s = \sigma_c^2 / \langle c_{\text{NO}_x} \rangle$, remains approximately constant after the first 1.5 meters of dispersion ($\sqrt{I_g^c} = 0.5 \pm 0.15$); this is the only direct information concerning σ_c^2 and I_s in the available data. The approximately constant value of the segregation suggests that, in the downwind range of available measurements, the floor of the wind tunnel does not affect the variance significantly, at least close to source height, and allows the estimation of a constant value of ω (in terms of p and A_1). A value of $A_1 = 3p$ is assumed for the calculations according to the analysis for constant I_g^c and self-similarity of variance profiles (Chapter 5), and this choice determines directly the value of ω . However, as will be discussed in the next section, extensive calculations for varying values of the parameters show the

overall effect of the exact choice (within their acceptable range) of A_1 (as well as of α) on the final results of the TRPM to be only minor, at least under the conditions of the present study. The same was found to be true for the I_s^c varying within its limits of uncertainty.

Another problem related to modeling σ_c^2 is the description of its evolution towards the profile given by (3.3-2) (which for constant ω and $\alpha \simeq 0$ reduces to a self similar form). This is a major problem in the fluid mechanical analysis of plume segregation and no general answer is known. However, the assumptions leading to the construction of the TRPM in its current form are associated with an artificial description of the evolution of segregation to which we will conform here. Indeed, in the formulation of the TRPM it is assumed that initially O_3 has a uniform concentration everywhere, i.e. it exists even in the source gases at its background concentration. This approximation is justified by the very large difference between the source concentration of NO and the background concentration of O_3 (3900 ppm versus 0.35 ppm in the present case). Obviously, the overall conversion of NO downwind will only be negligibly affected by the fictitious amount of O_3 that was assumed present in the emissions, and which will be practically consumed during a very short time interval after emission. Thus, in our approach the segregation is seen as induced by the chemistry very close to the source. So, as a first approximation, we assume that

$$\frac{\sigma_c}{\langle c_{NO_x} \rangle} = I_s^{1/2} \sim \frac{\langle c_{NO_2} \rangle}{\langle c_{NO_x} \rangle}$$

and for constant background ozone concentration $\langle c_{O_3} \rangle^{\text{env}}$

$$\frac{\sigma_c}{\langle c_{NO_x} \rangle} \sim 1 - \exp(-k_3 \langle c_{O_3} \rangle^{\text{env}} t)$$

which presents $\sqrt{I_s}$ as evolving towards its final value with a characteristic e-folding time determined by chemistry. (One must notice here that this chemical time scale $k_3 \langle c_{O_3} \rangle^{\text{env}}$ equals 2.5 times the Lagrangian integral time scale estimated for the wind tunnel experiments, an indication of the fact that chemical and macromixing processes proceed at rates of comparable magnitude). It should be kept in mind that the

preceding approach is introduced for consistency with the complete set of approximations involved in the TRPM and it is *not* aimed at explaining the details of the actual processes of mixing of point source plumes; it is a useful scheme for the specific purposes of the present reacting plume simulation and under the aforementioned restriction of very large concentration differences. From a practical viewpoint, calculations show that only the assumption of a characteristic time scale $k_3 \langle c_{O_3} \rangle^{\text{env}}$ for the attainment of the values given by (3.3-2) plays a significant role in the overall TRPM results. Indeed, the difference obtained from assuming $\sqrt{I_g^c}$ increasing according to the above "1-exp" law and from assuming e.g. $\sqrt{I_g^c} \sim t$ or $\sqrt{I_g^c} \sim \sqrt{t}$ was negligible for practical purposes.

At this point it is useful to discuss some aspects of the process of plume mixing and clarify the relevance of certain assumptions involved in our approach. Actual sources deviate from the idealization of the "point" concept in the initial phases of dispersion, even in the highly simplified case when emissions do not differ in momentum or buoyancy from the ambient turbulent flow, because the finite dimensions of the source obviously dictate a separate initial flow that merges gradually with the ambient. During this process of flow merging the background ozone must diffuse through the plume boundaries and mix down to the molecular level with the NO rich regions in order that chemical reactions occur. As turbulent dispersion processes mix the plume with the background air a "macromixed zone" in which both NO and O₃ are present – in the sense that their mean concentration values are nonzero – is created near the plume boundaries. O₃ is diffusing from the plume edges inwards but is largely consumed by NO before the centerline is reached and NO₂ peaks will be formed in the macromixed zone, which at any given plume cross-section will have the form of a ring whose outer circle defines the reacting plume boundaries (Hegg et al., 1977). The width of this ring increases downwind until it covers the entire cross-section of the plume and the NO₂ peaks eventually disappear (see Figure 3 - 3).

In Builtjes' experiments such NO₂ peaks were observed very close to the source (although the scatter of the data does not allow quantitative estimates of the magni-

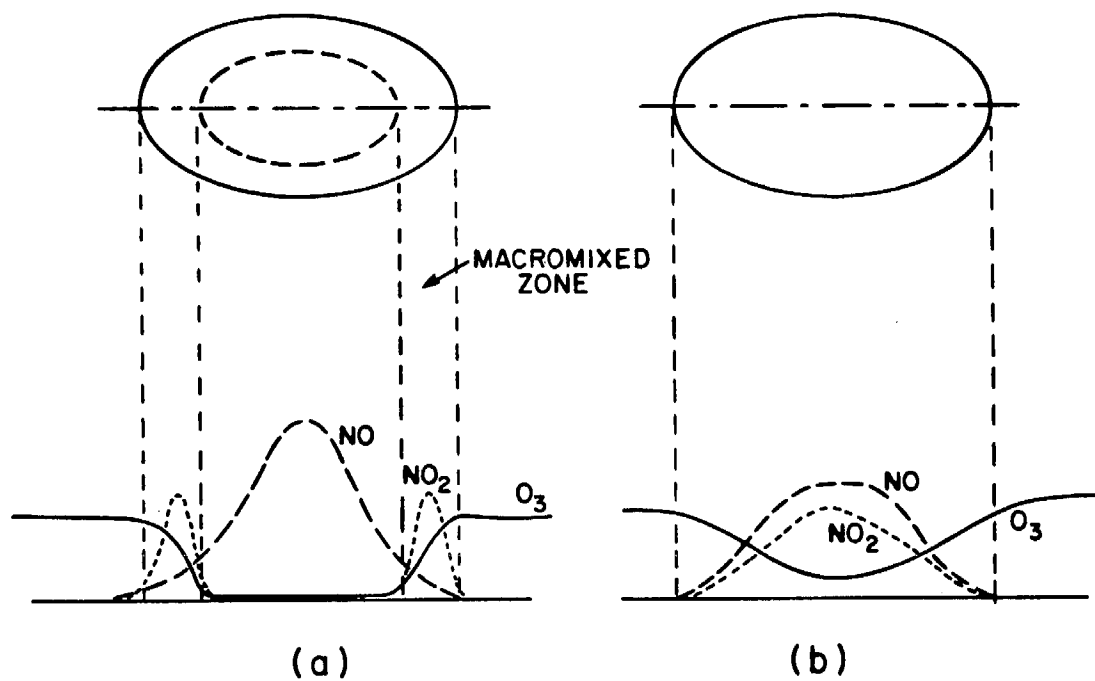


Figure 3-3
Evolution of Macromixing in a NO Plume:
Mean Profiles of NO, NO₂ and O₃
at Two Downwind Distances.

tude and position of these peaks); nevertheless this ring-type structure disappears in the first 2 meters of the plume dispersion. Builtjes (1983) notes that for practical applications it is not necessary to use a model that is capable of calculating the observed NO₂ peaks, although it should be able to estimate the retardation in the reaction rate caused by incomplete macromixing and micromixing in the atmospheric dispersion phase of plume evolution. This suggestion was adopted in the present version of the TRPM and source size effects are neglected, based on the fact that the details of the initial merging process will have negligible effects on the overall conversion of NO to NO₂ that is observed further downwind.

3.3.3 The TRPM Equations

The equation governing the NO-NO₂-O₃ system under the assumptions stated, and for the specific conditions relevant to the data base described, assumes the form

$$\begin{aligned} \bar{u} \frac{\partial \langle \xi \rangle}{\partial x} - K_y(x) \frac{\partial^2 \langle \xi \rangle}{\partial y^2} - K_z(x) \frac{\partial^2 \langle \xi \rangle}{\partial z^2} = \\ = \tilde{R}_1(x, y, z) \langle \xi \rangle^2 + \tilde{R}_2(x, y, z) \langle \xi \rangle + \tilde{R}_3(x, y, z) \end{aligned} \quad (3.3 - 3)$$

(or, in compact form, $\mathcal{L}_K^M = \tilde{R}$) where

$$K_i(x) = \frac{\bar{u}}{2} \frac{d\sigma_i^2}{dx} \quad (3.3 - 4)$$

and

$$\begin{aligned} \tilde{R}_1 &= k_3(1 + I_s) \\ \tilde{R}_2 &= k_3 \langle c_{NO_s} \rangle (1 + I_s) + k_3 \langle c_{O_s} \rangle^{\text{env}} \\ \tilde{R}_3 &= k_3 \langle c_{NO_s} \rangle \langle c_{O_s} \rangle^{\text{env}} \end{aligned} \quad (3.3 - 5)$$

with $\langle c_{NO_s} \rangle$ and σ_c^2 given by (3.3-1) and (3.3-2) respectively.

Here $\langle \xi \rangle$ is the *local phenomenal extent* of reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (Chapter 2), and for the specific experimental system under consideration

$$\langle c_{NO_2} \rangle = \langle \xi \rangle, \quad \langle c_{NO} \rangle = \langle c_{NO_s} \rangle - \langle \xi \rangle, \quad \langle c_{O_s} \rangle = \langle c_{O_s} \rangle^{\text{env}} - \langle \xi \rangle \quad (3.3 - 6)$$

The boundary conditions associated with (3.3-3) are

$$\langle \xi \rangle = 0 \text{ at } (x, y, z) = (0, y, z) \quad (3.3-7)$$

$$\langle \xi \rangle \rightarrow 0 \text{ at } y \rightarrow \pm\infty, z \rightarrow \infty, \quad \frac{\partial \langle \xi \rangle}{\partial z} = 0 \text{ at } z = 0 \quad (3.3-8)$$

Numerical solutions of (3.3-3) were obtained through

- (i) an Alternating Direction Implicit (ADI) finite difference scheme, and,
- (ii) through iterative solution of the associated integral equation.

The ADI method is especially suitable for the problem described by (3.3-3) since the nonlinearity appears only in the kinetic term. This term is calculated directly in each step using the value of $\langle \xi \rangle$ estimated in the immediately preceding iteration, performed in the alternative direction. The simple geometry of the simulated experimental system and the homogeneous boundary conditions also allow a reduction of the computational burden because of the existing symmetry with respect to the $(x, 0, z)$ plane. Thus, calculations for each x -step only have to be performed in, say, the positive $(y, 0, z)$ half-plane under the restriction $\partial \langle \xi \rangle / \partial y = 0$ at $y = 0$. (The basic finite-difference equations for the present calculations are summarized in Appendix A3.1).

The alternative choice of a feasible iterative point solution is allowed by the fact that, in the case under consideration, analytical expressions are available for all the parameters involved in (3.3-3), and the analytical form $G^M(x, y, z|x', y', z')$ of the Green's function of the partial differential operator/boundary conditions of (3.3-3) is known:

$$G^M(x, y, z|x', y', z') = \frac{1}{2\pi\sigma_y(x-x')\sigma_z(x-x')\bar{u}} \exp \left[-\frac{(y-y')^2}{2\sigma_y^2(x-x')} - \frac{(z-z')^2}{2\sigma_z^2(x-x')} \right] \quad (3.3-9)$$

Using as an initial first approximation for $\langle \xi \rangle$ the value corresponding to the pseudo-linear version of the problem, i.e. the solution obtained under the assumption that the mean ozone concentration remains everywhere constant at its background value,

$$\langle \xi \rangle^{(0)}(x, y, z) = \langle c_{NO_x} \rangle [1 - \exp(-k_3 \langle c_{O_3} \rangle^{\text{env}})] \quad (3.3-10)$$

one obtains a first approximation for \tilde{R} :

$$\tilde{R}^{(0)}(\langle \xi \rangle; x, y, z) = \tilde{R}(\langle \xi \rangle^{(0)}; x, y, z)$$

The next approximation for $\langle \xi \rangle$ is obtained through

$$\langle \xi \rangle^{(1)}(x, y, z) = \int_0^x \left[\int_{-\infty}^{\infty} \int_0^{\infty} G^M(x, y, z | x', y', z') \tilde{R}(\langle \xi \rangle^{(0)}; x', y', z') dz' dy' \right] dx' \quad (3.3-11)$$

and so on, until convergence to a steady value of $\langle \xi \rangle$ is obtained.

3.4 RESULTS AND DISCUSSION

In this section we present results of the numerical calculations compared with the experimental data of Builtjes (1981). The most important comparisons are presented in Figures 3-4 and 3-5 that refer to calculations and measurements along the centerline of the plume. Both calculations and data are presented in dimensionless form, as ratios of concentrations, and therefore give directly the dependence of conversions on downwind distance or travel time. The farthest downstream available measurements in the wind tunnel were taken at 5 m, which at a wind speed of 0.4 m/s corresponds to a travel time of 12.5 s. The respective quantities for a field situation would be approximately a 2.5 km downwind distance (or 7.5 min of travel time) with an average wind speed of 5.7 m/s.

Figure 3-4 contains the measured values of the ratio of NO to total NO_x as well as three calculated curves:

- (a) *turbulent kinetics calculations*, of $\langle c_{\text{NO}} \rangle / \langle c_{\text{NO}_x} \rangle$ i.e. results from the TRPM considering the effects of both macromixing and micromixing, with parameters estimated as described in the previous section,
- (b) *conventional kinetics calculations*, i.e. results from the common reaction-diffusion equation (to which the TRPM reduces for $I_s = 0$), that incorporate solely the effects of macromixing, and,
- (c) *modified Gaussian plume calculations*, i.e. results from the pseudo-linear reaction assumption (equation (3.3-10)) which views plume macromixing in a very simplistic manner, that is with ozone profiles unaffected by the plume, and, of course, ignores micromixing effects. The same dispersion parameters were used in all the three different models. The 50% conversion time predicted by the TRPM is 9.0 s (of the order of 5.3 min for the comparable field situation), in very good agreement with the wind tunnel measurements. The respective calculations from the conventional reaction-diffusion equation gave a 50% conversion time equal to 6.5 s (3.8 min in the field

situation), i.e. about 28% shorter than the observed time, and the modified Gaussian plume model predicted 4.75 s (2.8 min in the field), that is almost 47% less than the observed value.

Figure 3-5 shows the measurements of the ratio of O_3 concentration (under reactive conditions) to the corresponding background value along the centerline, again compared with calculations that assume turbulent and conventional kinetics. (The relevant assumption of the modified Gaussian plume model is that $\langle c_{O_3} \rangle = \langle c_{O_3} \rangle^{\text{env}}$ and the ratio shown in Figure 3-5 is always unity). The narrow peak of the calculated results at the origin arises from the assumption $\langle c_{O_3} \rangle = \langle c_{O_3} \rangle^{\text{env}}$ for all (y, z) at $x = 0$ that was discussed in the previous section; the fast descent of the calculated ratio to a near zero value serves as an a posteriori justification of this approximation.

Comparisons of the transverse profile measurements and calculations are presented in Figures 3-6a to 3-6e for downwind distances 1, 2, 3, 4 and 5 m. The O_3 data were selected as being the more reproducible and less scattered. Again dimensionless ratios of concentrations are given, for easier comparison with other situations, plotted against the dimensionless distance y/σ_y from the plume centerline. The corresponding numerical solutions of the reaction-diffusion equation with conventional kinetics are also given in these figures. Although the scatter of the transverse data is significant, Figures 3-6a to 3-6e corroborate the basic conclusion arising from the comparison presented in Figures 3-4 and 3-5, i.e. that the TRPM indeed can provide a quantitative estimate of the effects of both macro- and micro- mixing on the evolution of plume reactions.

The primary parameters implicit in the calculations presented in the above figures were either

- (a) measured, or estimated so as to fit dispersion measurements (σ_y , σ_z or the exponent p),
- (b) the "most typical" among possible alternatives, corresponding to first-choice conventions of the peripheral models employed (i.e. $A_1 = 3p$), or
- (c) the average values of randomly fluctuating quantities that were measured in the

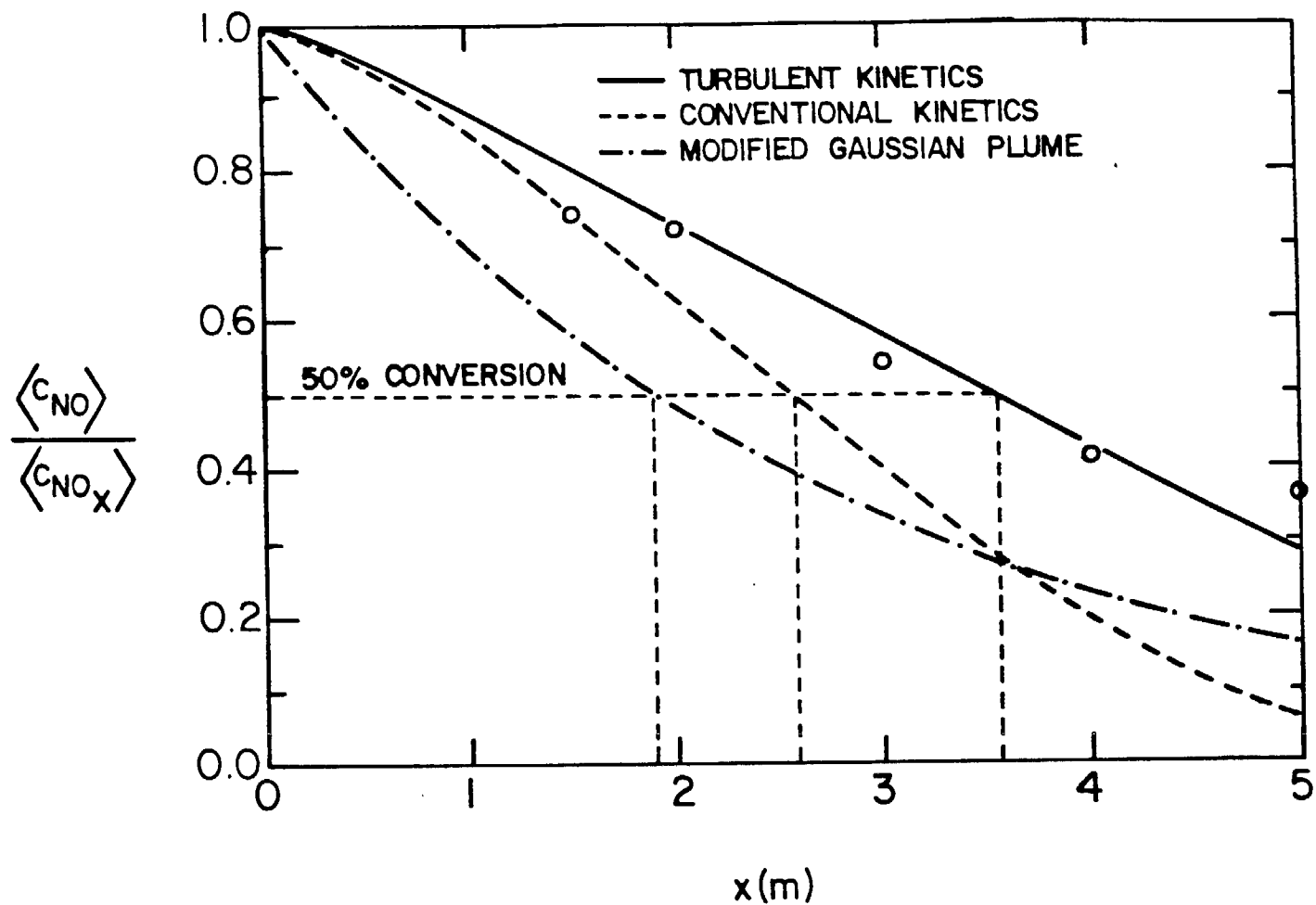
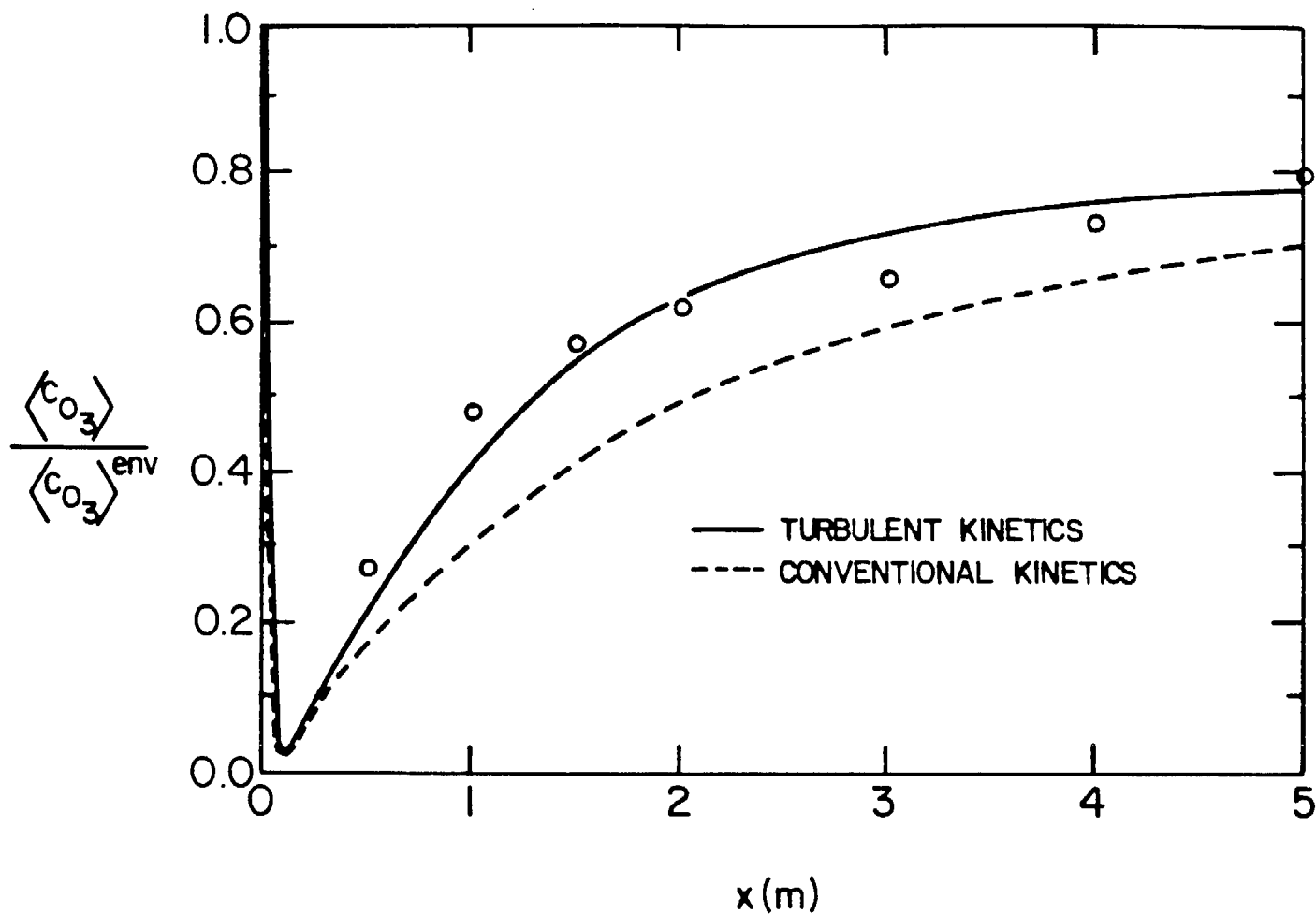


Figure 3-4

Ratio of NO to Total NO_x Concentration along the Plume Centerline:

Data of Builtjes (1981) and Calculations

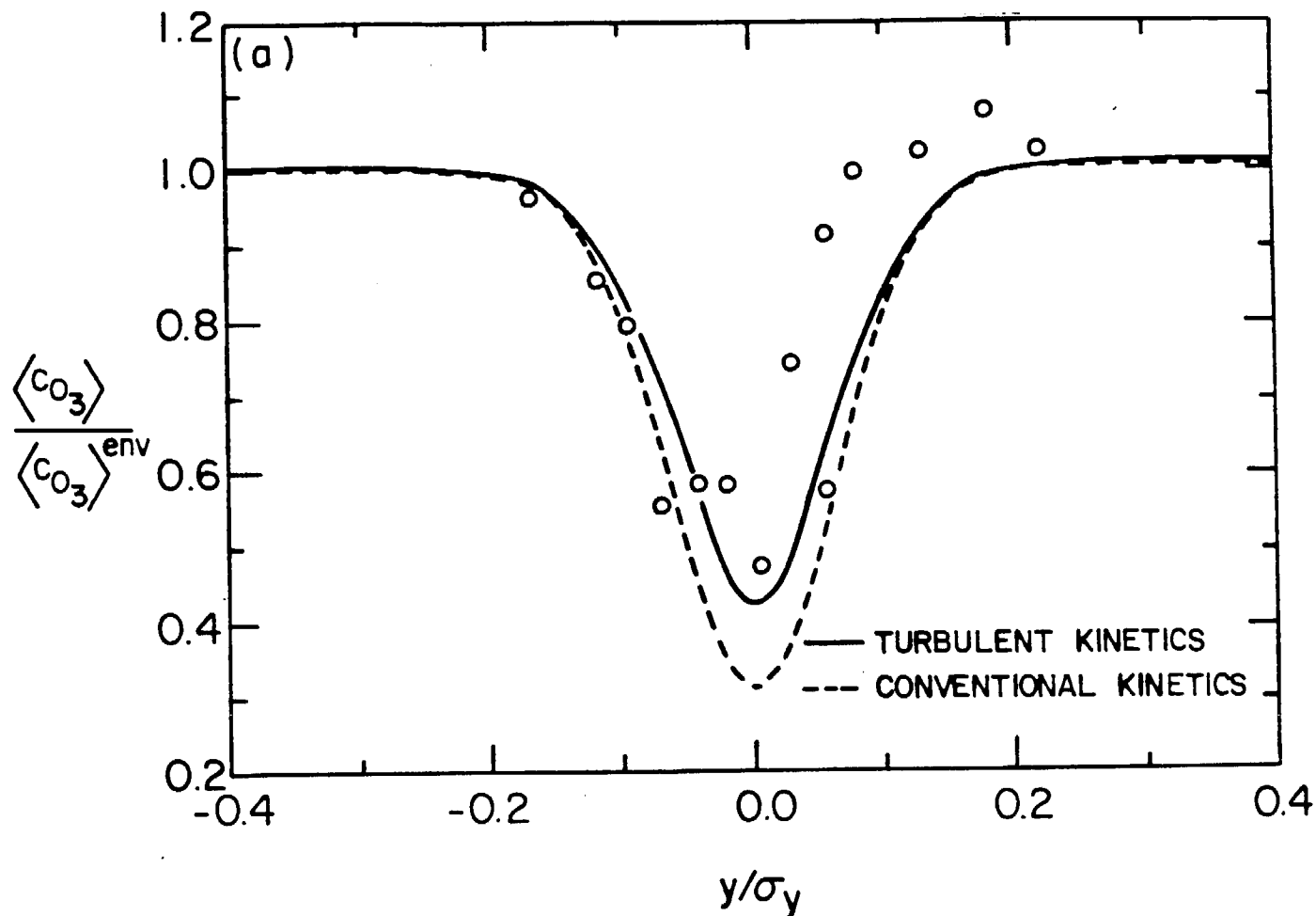
- (i) for Turbulent Kinetics (the complete TRPM equations),
- (ii) for Conventional Kinetics (ignoring the effects of micromixing), and
- (iii) from a Modified Gaussian Plume Model.

**Figure 3-5**

Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$) along the Plume Centerline:

Data of Builtjes (1981) and Calculations

- (i) for Turbulent Kinetics (the complete TRPM equations), and
- (ii) for Conventional Kinetics (ignoring the effects of micromixing).

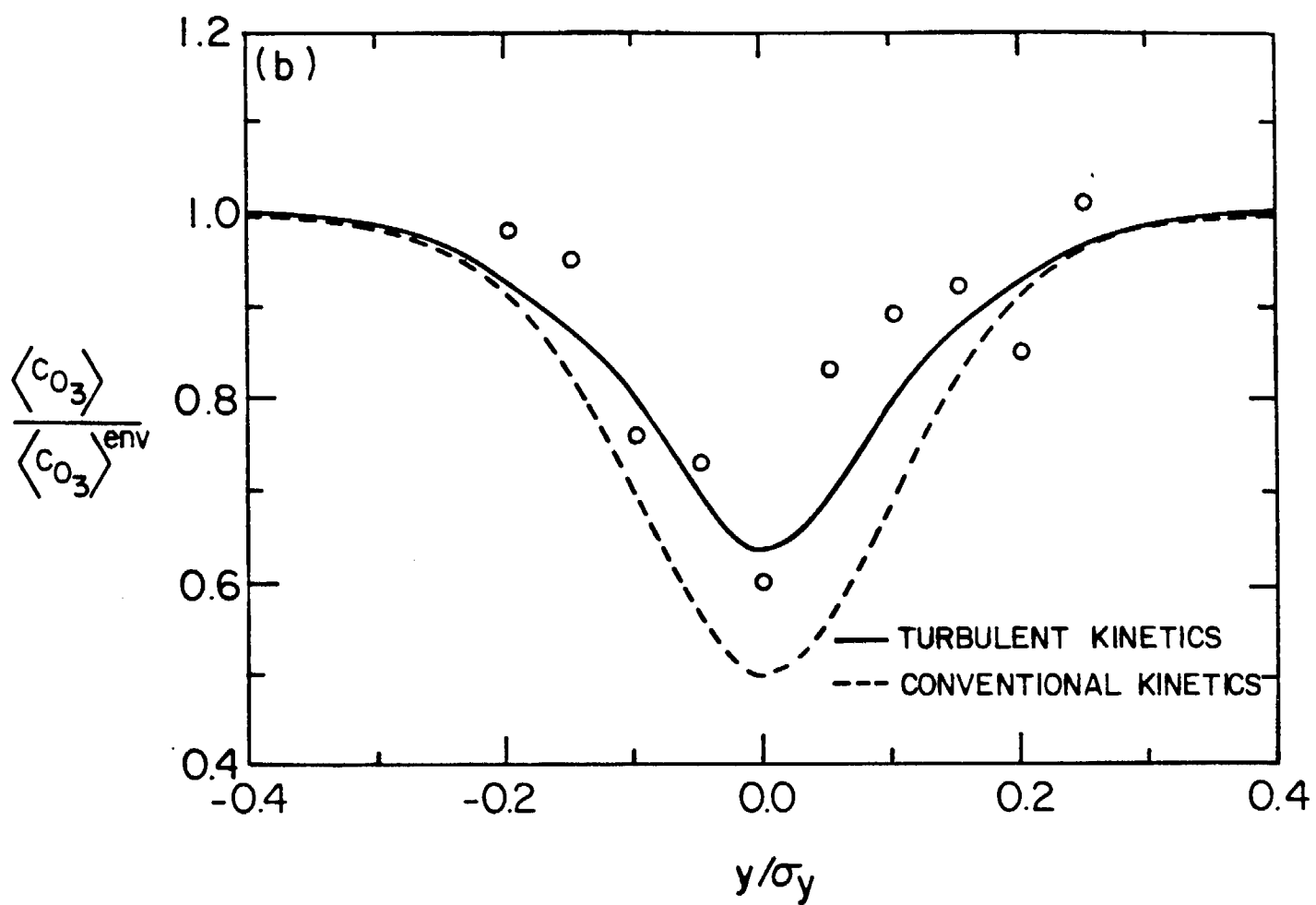
**Figure 3-6a**

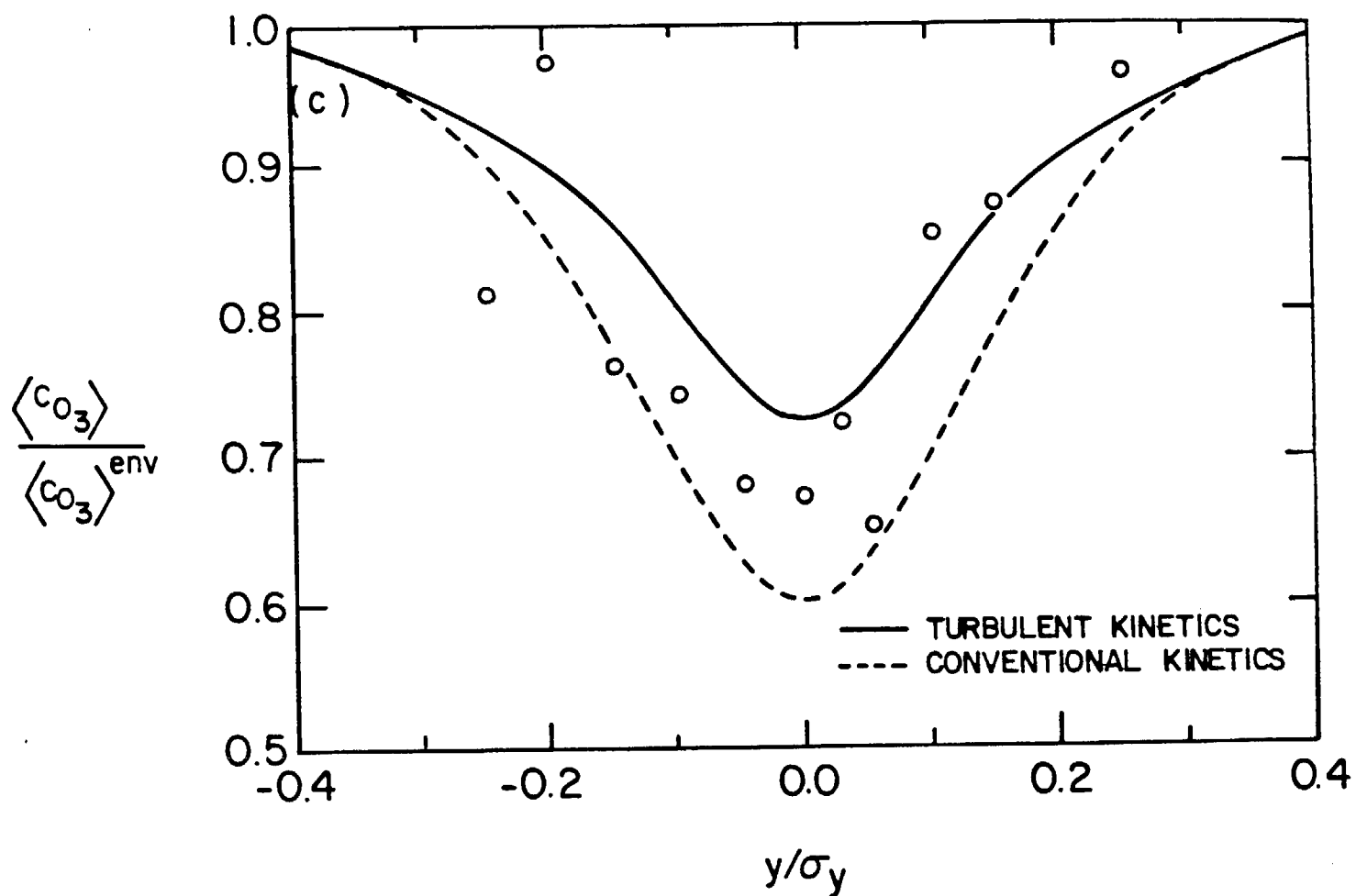
Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$)

Horizontally at Source Height at $x = 1$ m Downwind:

Data of Builtjes (1981) and Calculations

- (i) for Turbulent Kinetics (the complete TRPM equations), and
 - (ii) for Conventional Kinetics (ignoring the effects of micromixing)
- vs the Dimensionless Distance y/σ_y from the Centerline.

**Figure 3-6b**As in Figure 3-6a, at $x = 2$ m

**Figure 3-6c**As in Figure 3-6a, at $x = 3$ m

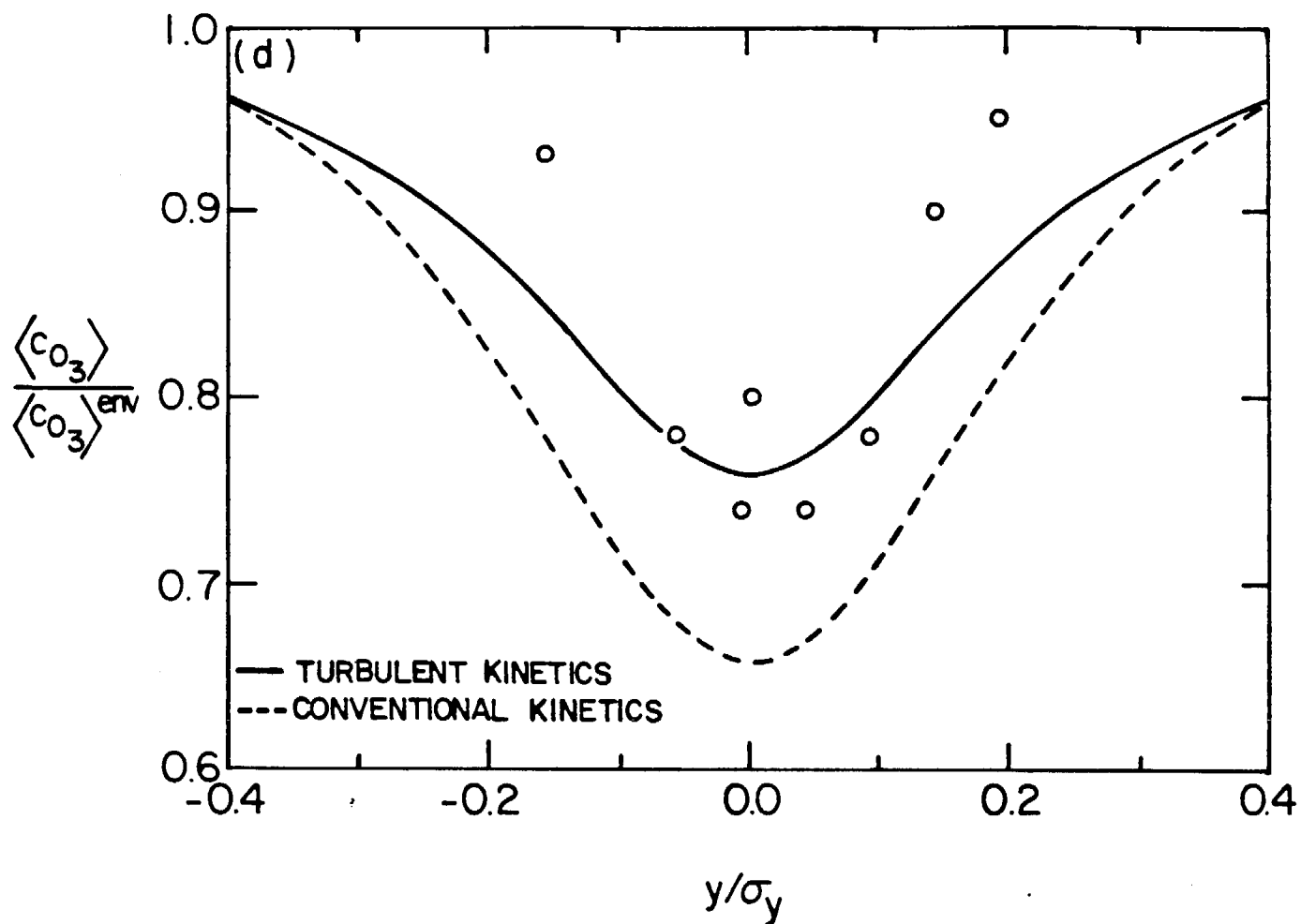
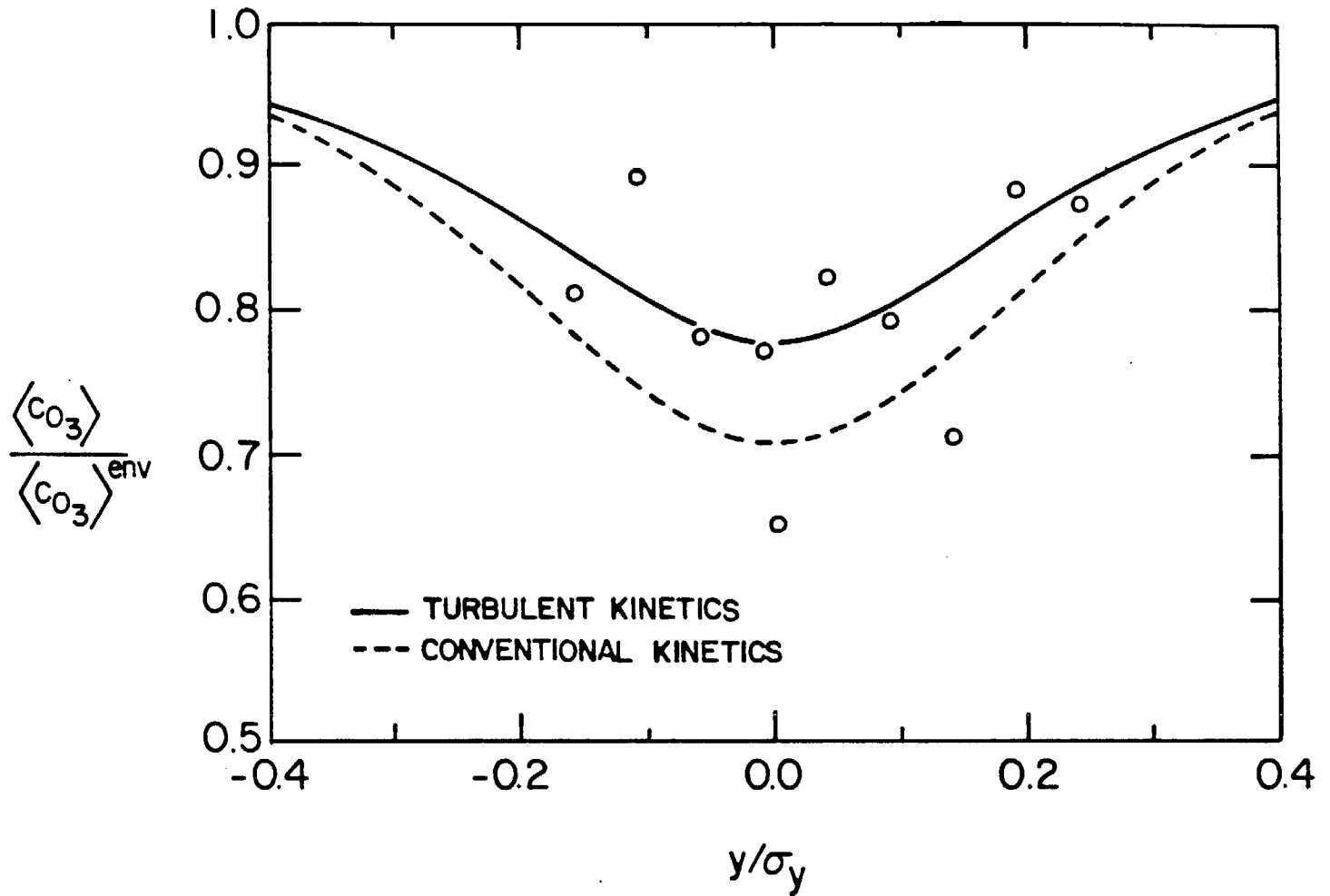


Figure 3-6d

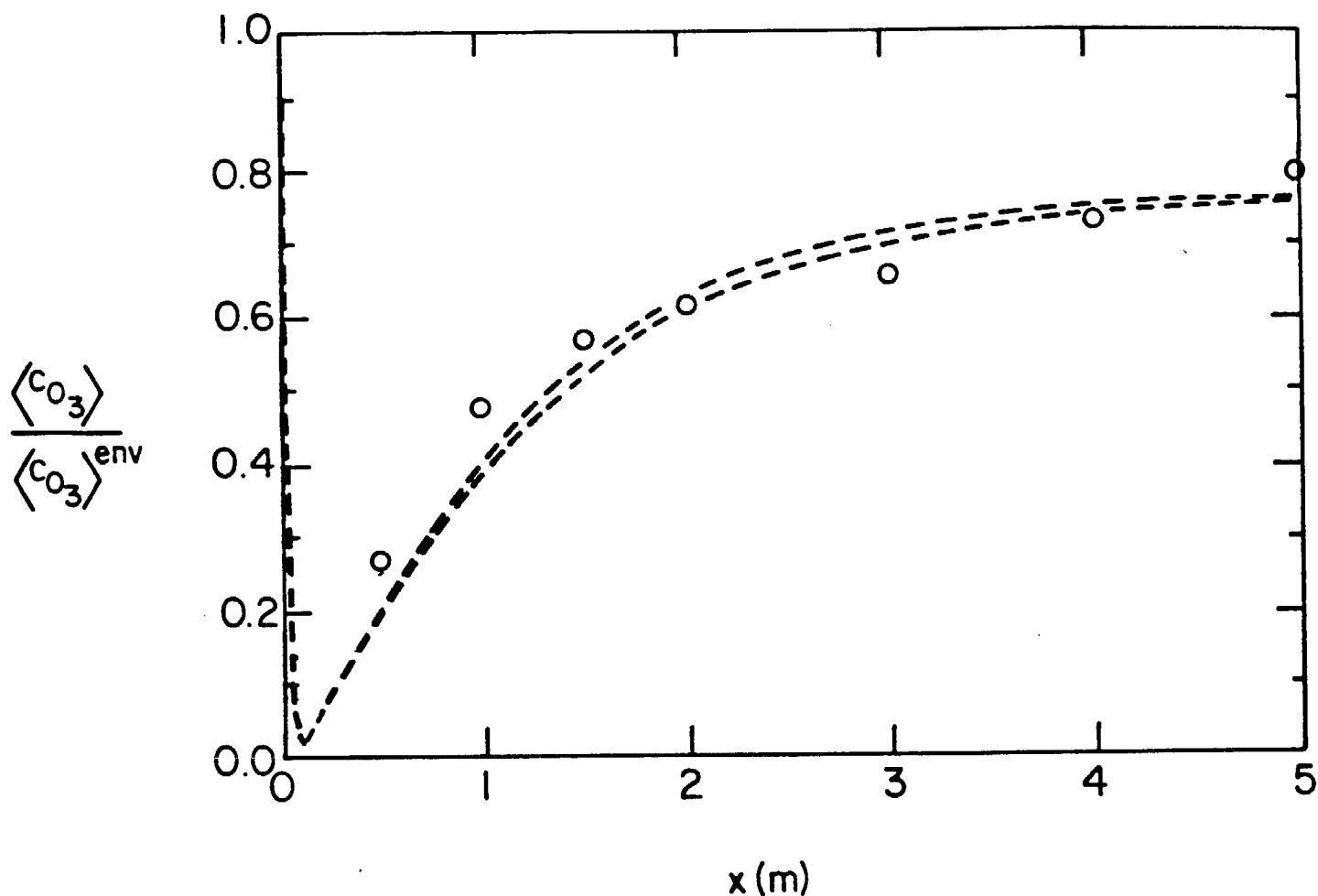
As in Figure 3-6a, at $x = 4$ m

**Figure 3-6e**As in Figure 3-6a, at $x = 5$ m

wind tunnel (e.g. the average temperature in the wind tunnel was used to calculate the rate coefficient k_3 and the average value of centerline intensity of segregation I_g^c was used to fix parameters in the segregation profiles).

Extensive sets of calculations were performed for varying values of the primary parameters, especially for those in categories (b) and (c) above, in order to assess the sensitivity of the TRPM to their values. The results of these calculations show that the TRPM is quite robust with respect to the parameters involved and allows for a reasonable amount of uncertainty in their estimation; they further show that the present agreement between measurements and theoretical predictions does not arise from any type of "fine tuning" of parameters. As an example, the effect of $\sqrt{I_g^c}$ variation between its extreme observed values in the steady state range (approximately 0.35 to 0.65), is shown in Figure 3-7: the calculations are for the $\langle c_{O_s} \rangle / \langle c_{O_s} \rangle^{\text{env}}$ ratio, as those in Figure 3-5, with measured values also shown, and the two curves correspond to the minimum and maximum measured value of I_g^c . The analogous calculation is shown in Figure 3-8 for the dissipation factor A_1 varying within its entire range of values, as reported in the literature for various flows, i.e. between 1.5 and 3.0. (The calculations of Figure 3-5 were performed with $A_1 = 3p = 2.72$). Another point that is worthy of mentioning is that calculations with the complete TRPM are less sensitive to random variations of the chemical rate coefficients, due e.g. to random variations in temperature or in light intensity, than calculations employing conventional kinetics. This of course is to be expected, since, in the case of turbulent kinetics, chemistry has to "share" the control of the system with the mixing processes. Figures 3-9a and 3-9b show the effect of varying k_3 on both turbulent and conventional kinetics calculations.

Finally, in order to provide a more general perspective, the theoretical predictions of the $\langle c_{O_s} \rangle / \langle c_{O_s} \rangle^{\text{env}}$ ratio for the reaction $O_3 + NO \rightarrow NO_2 + O_2$, again from numerical solution of the reaction-diffusion equation for both turbulent and conventional kinetics, are compared with results that incorporate the reverse reaction (with a constant average k_1), with all other parameters identical,

**Figure 3-7**

Sensitivity of TRPM Calculations to the Intensity of Plume Segregation:

Calculations of the Ratio

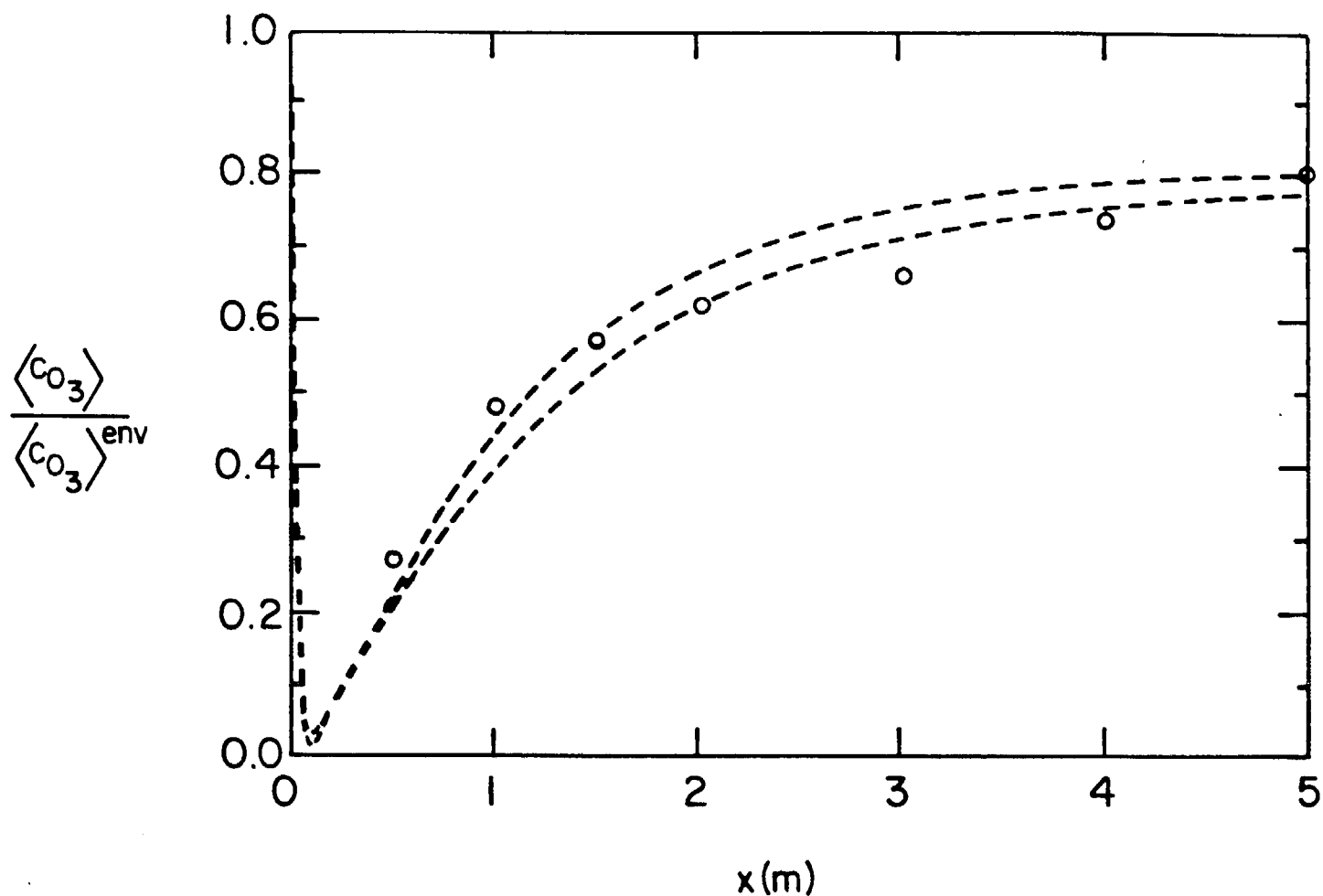
of O_3 Concentration (under reactive conditions)

to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$)

along the Plume Centerline

for $\sqrt{I_s^c} = 0.65$ (upper curve) and for $\sqrt{I_s^c} = 0.35$ (lower curve)

(Data of Builtjes (1981))

**Figure 3-8**

Sensitivity of TRPM Calculations to the Dissipation of Fluctuations Scale Factor:

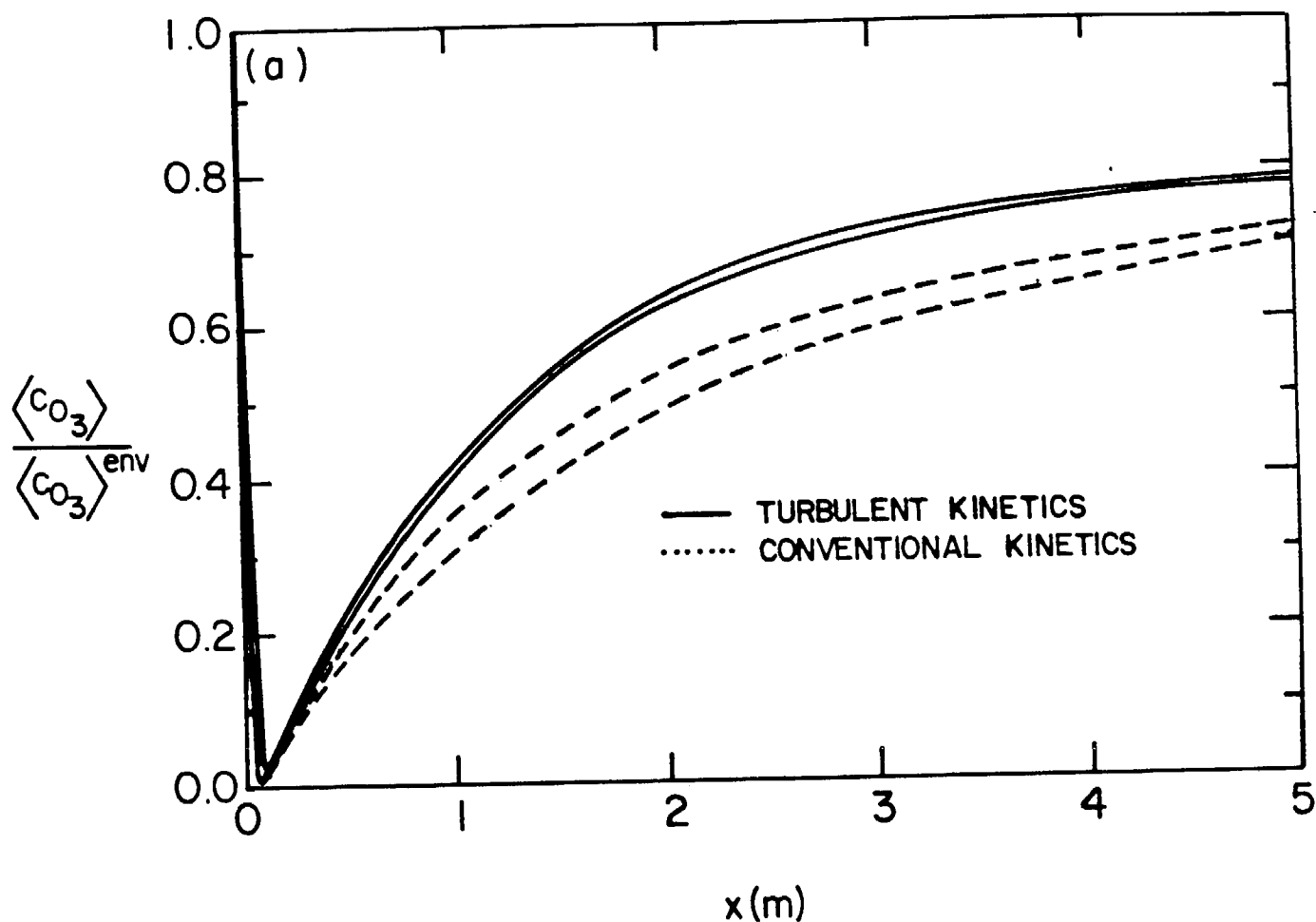
Calculations of the Ratio

of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$)

along the Plume Centerline

for $A_1 = 1.5$ (upper curve) and for $A_1 = 3.0$ (lower curve)

(Data of Builtjes (1981))

**Figure 3-9a**

Sensitivity of Turbulent and Conventional Kinetics Calculations

to the Reaction Rate Constant:

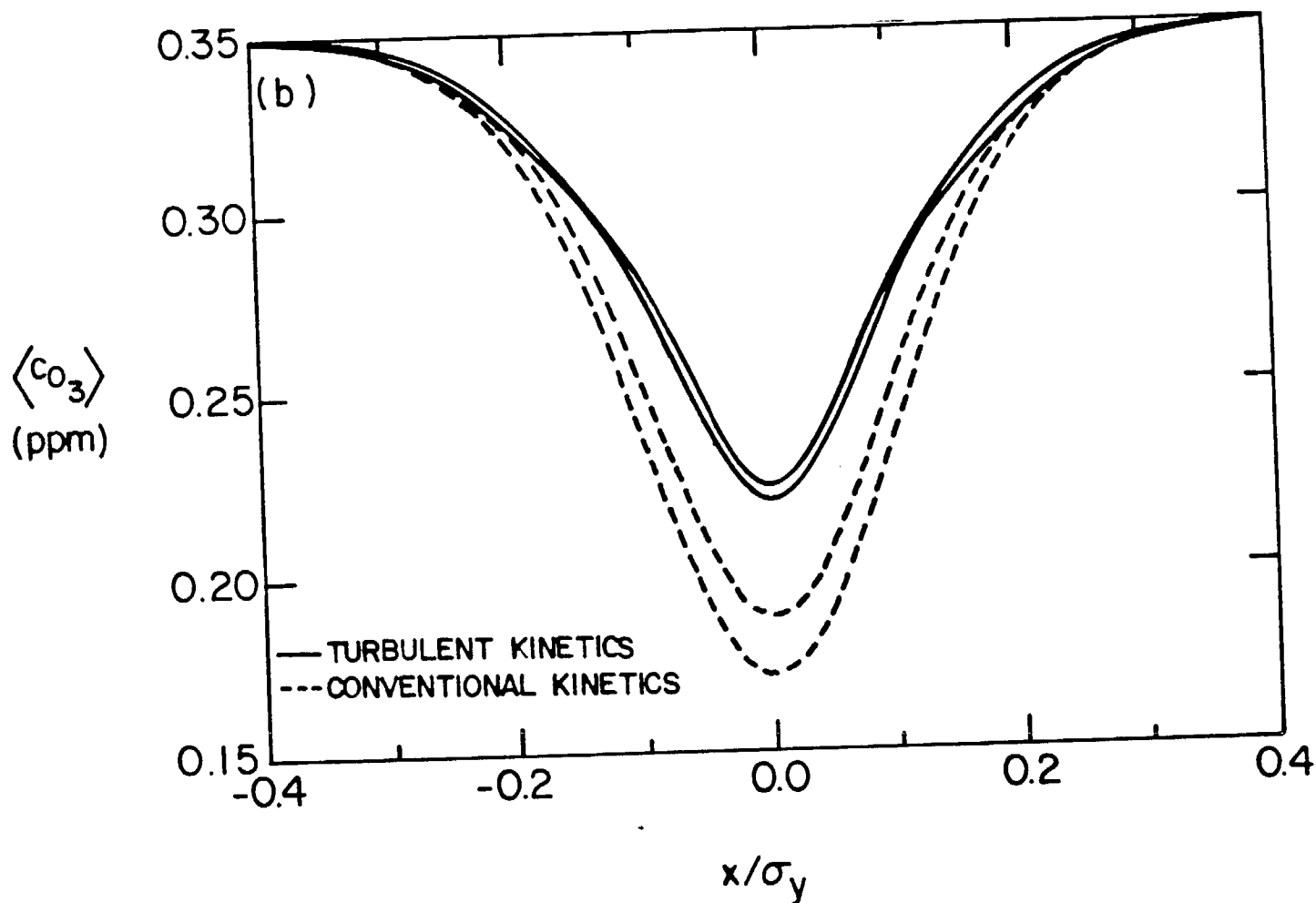
Calculations of the Ratio of O_3 Concentration (under reactive conditions)

to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$)

along the Plume Centerline

for $k_3 = 0.36 \text{ ppm}^{-1} \text{ s}^{-1}$ (upper solid and dashed curves)

and for $k_3 = 0.44 \text{ ppm}^{-1} \text{ s}^{-1}$ (lower solid and dashed curves)

**Figure 3-9b**

Sensitivity of Turbulent and Conventional Kinetics Calculations to
the Reaction Rate Constant:

Calculations of the Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$),

Horizontally at Source Height and at $x = 2$ m,

for $k_3 = 0.36 \text{ ppm}^{-1} \text{ s}^{-1}$ (upper solid and dashed curves)

and for $k_3 = 0.44 \text{ ppm}^{-1} \text{ s}^{-1}$ (lower solid and dashed curves).

- (a) from solution of the reaction-diffusion equations exactly as before but incorporating the new kinetic term, and,
- (b) from assuming photostationary equilibrium and applying $\tilde{R} = 0$ (Figure 3-10).

These calculations show that, under conditions such as those prevailing in the reactive plume experiments of Builtjes, photostationary equilibrium is an acceptable approximation only after travel times of about 15 s at the wind tunnel scale (at which time micromixing effects also become negligible). Close to the source, where the concentration of NO is 4 or 5 orders of magnitude higher than that of the background O₃, a requirement for equilibrium induces a significant increase of the reaction rate. However, this increase cannot be observed in reality, because the rate of mixing would then constitute a much slower step and would control the overall process. The (hypothetical) variation of the photostationary state parameter along the plume centerline under the assumption of local equilibrium with turbulent kinetics is shown in Figure 3-11.

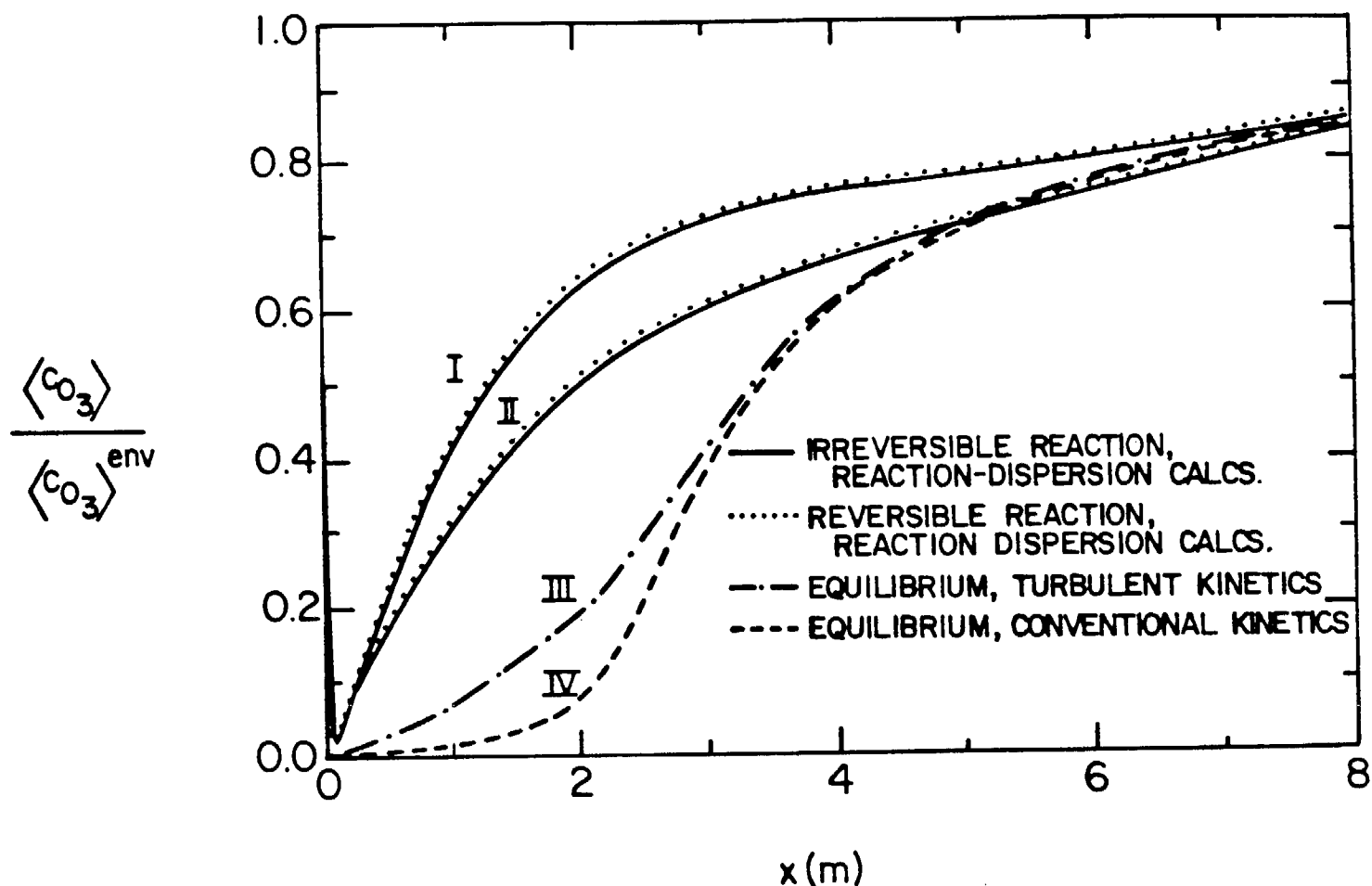


Figure 3-10

Effect of the Reverse Reaction $NO_2 \rightarrow NO + O$

on the Calculations of Figure 3-5:

- (I) Turbulent Kinetics Reaction-Dispersion calculations
- (II) Conventional Kinetics Reaction-Dispersion Calculations
- (III) Photostationary Equilibrium Approximation with Turbulent Kinetics
- (IV) Photostationary Equilibrium Approximation with Conventional Kinetics ($\lambda = 1$)

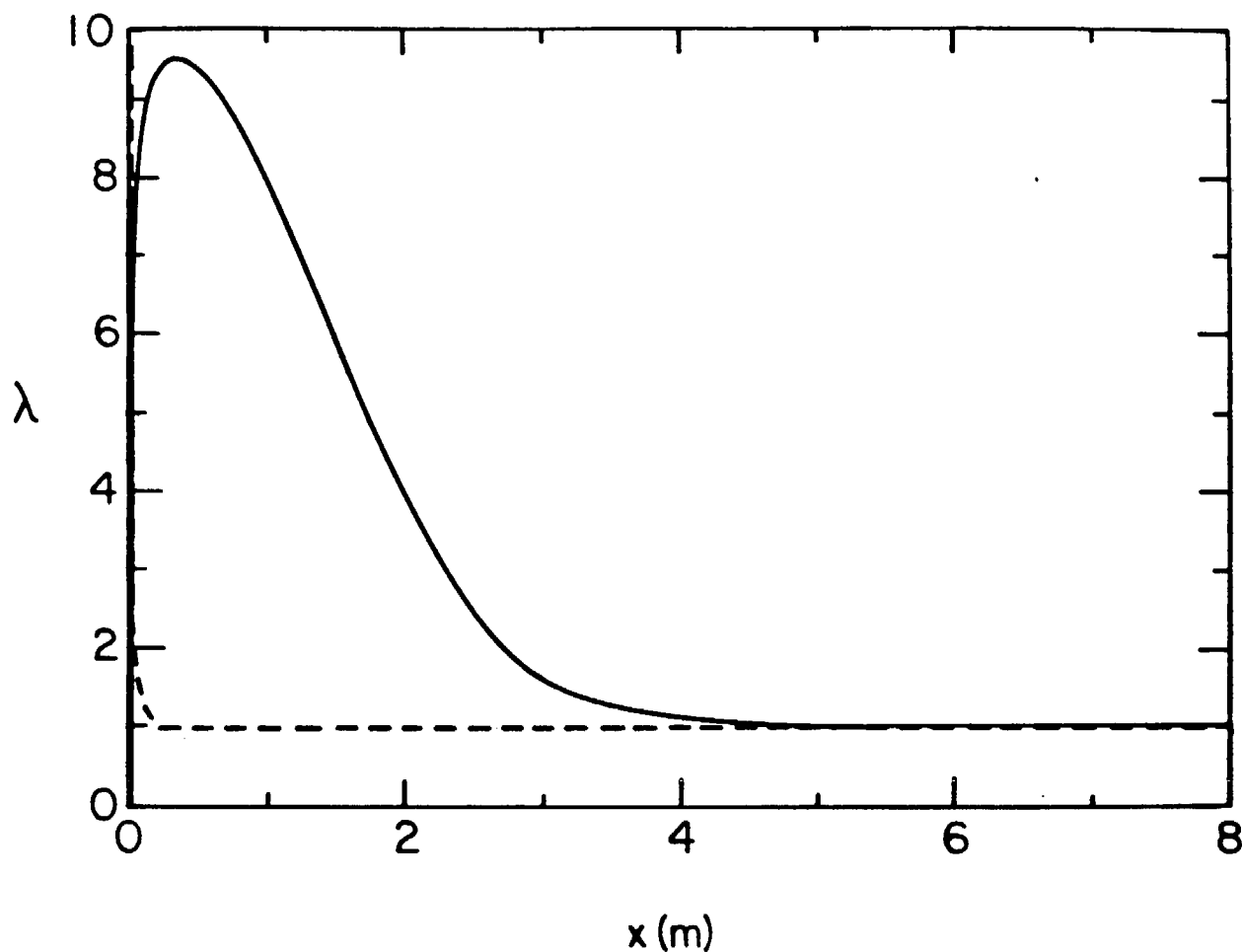


Figure 3-11

Variation of the Photostationary State Parameter λ along the Plume Centerline
(under the assumption of photostationary equilibrium with turbulent kinetics)
for Emission Conditions as in Builtjes (1981) Experiments

3.5 CONCLUSIONS

Comparisons with experimental data indicate that the TRPM (described in Chapter 2) represents the processes of simultaneous plume dispersion and reaction in a satisfactory manner. In particular it is worthy to note that the calculations show a definite lack of sensitivity with respect to the exact values of the physical parameters involved in the description of the effects of incomplete micromixing. Hence it seems possible that the TRPM could provide adequate estimates of these effects even with approximate values of these parameters.

Extension of the predictive capability of the model to much more complex situations, for example involving profound irregularities of the flow field (that cannot be treated as fluctuations of quantities with well behaved means), is in principle possible but will require use of more elaborate and computationally intensive versions of the TRPM than the one used for the calculations presented here, and, furthermore, will also demand inputs that are more complex and difficult to estimate.

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APPENDIX A3.1

**Alternating Direction Implicit
Finite Difference Form of (3.3-3)**

The results presented in Chapter 3 in comparison with the experimental data of Builtjes (1981) were obtained from numerical solution of (3.3-3) through an Alternating Direction Implicit (ADI) finite difference scheme which is the standard choice for solving the basic TRPM equations in its master module (the alternative is the iterative solution of the integral equation that is equivalent to the problem described by (3.3-3) and the associated side conditions).

The finite-difference grid spans the vertical plume cross-section and calculations are performed in alternative (vertical and horizontal) directions at each time step. The basic features of the ADI method are described in several standard references (see, e.g., Richtmyer and Morton, 1967; Ames, 1977; Lapidus and Pinder, 1982). The choice of this method for the solution of (3.3-3) is natural because the nonlinearity appears only in the chemical kinetics term and therefore can be handled easily in the calculations by introducing in the r.h.s. the value of $\langle \xi \rangle$ estimated in the iteration that is performed in the alternative direction. Furthermore, the special nature of the r.h.s. term in (3.3-3), which "spreads" the forcing function ("disturbance") in the entire three dimensional space makes the solution procedure less sensitive with respect to the discretization (and thus allows use of rather large steps in both space and time).

In the calculations the plume is assumed symmetric with respect to the vertical plane passing through the centerline; this allows reduction of the calculations to the half cross-section of the plume while imposing an artificial boundary condition on the vertical axis. (Moreover, in the very early stages of the atmospheric dispersion phase - see Chapter 7 - where the effects of the ground are negligible, the plume cross-section can also be assumed symmetric with respect to the horizontal plane passing through its center of mass. Then calculations can be performed in only a quadrant of the cross-section by imposing an artificial boundary condition on the horizontal axis as well.) The initial source concentration is assumed Gaussian (with maximum equal to the source concentration); this profile is used for the calculation of the starting \tilde{R}_i 's. At each time step these "turbulent kinetics functions" are estimated using the analytical expressions for the mean and variance of NO_x provided by the Gaussian and the LPF formulas respectively.

Let us for convenience set

$$a_{i,j}^k = \langle \xi(x = \bar{u}k\Delta t, y = i\Delta y, z = j\Delta z) \rangle$$

(and similarly use subscripts and superscripts to denote the values of \tilde{R}_i at each node of the plume cross-section and at each time step.

Further let

$$r_y = \frac{\Delta t K_y(x)}{(\Delta y)^2}, \quad r_z = \frac{\Delta t K_z(x)}{(\Delta z)^2}$$

and

$$\hat{r}_y = \frac{(\Delta y)^2}{K_y(x)}, \quad \hat{r}_z = \frac{(\Delta z)^2}{K_z(x)}$$

Then, the finite difference equations corresponding to the *specific* problem described by (3.3-3) and (3.3-7), (3.3-8) are:

Plume Interior

Odd Traverses

$$\begin{aligned} & a_{i,j}^{k+1} \left(\frac{1}{r_z} + 2 \right) - a_{i,j+1}^{k+1} - a_{i,j-1}^{k+1} = \\ & = \left(\frac{1}{r_z} - 2 \frac{r_y}{r_z} \right) a_{i,j}^k + r_y a_{i+1,j}^k + r_y a_{i-1,j}^k + \\ & + \hat{r}_z \left[\left(\tilde{R}_1 \right)_{i,j}^k (a_{i,j}^k)^2 + \left(\tilde{R}_2 \right)_{i,j}^k a_{i,j}^k + \left(\tilde{R}_3 \right)_{i,j}^k \right] \end{aligned} \quad (A3.1-1)$$

Even Traverses

$$\begin{aligned} & a_{i,j}^{k+2} \left(\frac{1}{r_y} + 2 \right) - a_{i+1,j}^{k+2} - a_{i-1,j}^{k+2} = \\ & = \left(\frac{1}{r_y} - 2 \frac{r_z}{r_y} \right) a_{i,j}^{k+1} + r_z a_{i,j+1}^{k+1} + r_z a_{i,j-1}^{k+1} + \\ & + \hat{r}_y \left[\left(\tilde{R}_1 \right)_{i,j}^{k+1} (a_{i,j}^{k+1})^2 + \left(\tilde{R}_2 \right)_{i,j}^{k+1} a_{i,j}^{k+1} + \left(\tilde{R}_3 \right)_{i,j}^{k+1} \right] \end{aligned} \quad (A3.1-2)$$

Boundaries

Free Boundary - Odd and Even Traverses

$$a_{i,j}^{\text{bound}} = 0 \quad (A3.1-3)$$

*Vertical Plane at y = 0**Odd Traverses*

$$\begin{aligned}
& a_{0,j}^{k+1} \left(\frac{1}{r_x} + 2 \right) - a_{0,j+1}^{k+1} - a_{0,j-1}^{k+1} = \\
& = \left(\frac{1}{r_x} - 2 \frac{r_y}{r_x} \right) a_{0,j}^k + 2r_y a_{1,j}^k \\
& + \hat{r}_x \left[\left(\tilde{R}_1 \right)_{0,j}^k (a_{0,j}^k)^2 + \left(\tilde{R}_2 \right)_{0,j}^k a_{0,j}^k + \left(\tilde{R}_3 \right)_{0,j}^k \right]
\end{aligned} \tag{A3.1-4}$$

Even Traverses

$$\begin{aligned}
& a_{0,j}^{k+2} \left(\frac{1}{r_y} + 2 \right) - 2a_{1,j}^{k+2} = \\
& = \left(\frac{1}{r_y} - 2 \frac{r_x}{r_y} \right) a_{0,j}^{k+1} + r_x a_{0,j+1}^{k+1} + r_x a_{0,j-1}^k + \\
& \hat{r}_y \left[\left(\tilde{R}_1 \right)_{0,j}^{k+1} (a_{0,j}^{k+1})^2 + \left(\tilde{R}_2 \right)_{0,j}^{k+1} a_{0,j}^{k+1} + \left(\tilde{R}_3 \right)_{0,j}^{k+1} \right]
\end{aligned} \tag{A3.1-5}$$

Horizontal Axis - Odd Traverses

$$\begin{aligned}
& a_{i,0}^{k+1} \left(\frac{1}{r_x} + 2 \right) - 2a_{i,1}^{k+1} = \\
& = \left(\frac{1}{r_x} - 2 \frac{r_y}{r_x} \right) a_{i,0}^k + r_y a_{i+1,0}^k + r_y a_{i-1,0}^k + \\
& + \hat{r}_x \left[\left(\tilde{R}_1 \right)_{i,0}^k (a_{i,0}^k)^2 + \left(\tilde{R}_2 \right)_{i,0}^k a_{i,0}^k + \left(\tilde{R}_3 \right)_{i,0}^k \right]
\end{aligned} \tag{A3.1-6}$$

Horizontal Axis - Even Traverses

$$\begin{aligned}
& a_{i,0}^{k+2} \left(\frac{1}{r_y} + 2 \right) - a_{i+1,0}^{k+2} - a_{i-1,0}^{k+2} = \\
& = \left(\frac{1}{r_y} - 2 \frac{r_x}{r_y} \right) a_{i,0}^{k+1} + 2r_x a_{i,0}^{k+1} + \\
& + \hat{r}_y \left[\left(\tilde{R}_1 \right)_{i,0}^{k+1} (a_{i,0}^{k+1})^2 + \left(\tilde{R}_2 \right)_{i,0}^{k+1} a_{i,0}^{k+1} + \left(\tilde{R}_3 \right)_{i,0}^{k+1} \right]
\end{aligned} \tag{A3.1-7}$$

Initial Node - Odd Traverses

$$\begin{aligned}
& a_{0,0}^{k+1} \left(\frac{1}{r_x} + 2 \right) - 2a_{0,1}^{k+1} = \\
& = \left(\frac{1}{r_x} - 2\frac{r_y}{r_x} \right) a_{0,0}^k + 2r_y a_{1,0}^k + \\
& + \hat{r}_x \left[\left(\tilde{R}_1 \right)_{0,0}^k (a_{0,0}^k)^2 + \left(\tilde{R}_2 \right)_{0,0}^k a_{0,0}^k + \left(\tilde{R}_3 \right)_{0,0}^k \right] \quad (A3.1-8)
\end{aligned}$$

Initial Node - Even Traverses

$$\begin{aligned}
& a_{0,0}^{k+2} \left(\frac{1}{r_y} + 2 \right) - 2a_{1,0}^{k+2} = \\
& = \left(\frac{1}{r_y} - 2\frac{r_x}{r_y} \right) a_{0,0}^{k+1} + 2r_x a_{0,1}^{k+1} + \\
& + \hat{r}_y \left[\left(\tilde{R}_1 \right)_{0,0}^{k+1} (a_{0,0}^{k+1})^2 + \left(\tilde{R}_2 \right)_{0,0}^{k+1} a_{0,0}^{k+1} + \left(\tilde{R}_3 \right)_{0,0}^{k+1} \right] \quad (A3.1-9)
\end{aligned}$$

In the problem (3.3-3), (3.3-7), (3.3-8) the horizontal axis is on the ground; however the equations (A3.1-1) to (A3.1-9) remain the same in the frame attached to the plume centerline (with obvious transformations in the \tilde{R} -terms).

When analytical solutions for the inert surrogate concentration and/or the internal plume variance are not available these quantities must be calculated numerically in order to be introduced in the \tilde{R} -terms of the equations for $\langle \xi \rangle$; the relevant partial differential equations are solved by a finite difference system that is similar to equations (A3.1-1) to (A3.1-9) but with the term containing the \tilde{R} 's equal to zero (for the mean concentration calculations) or replaced by the appropriate discrete form of the r.h.s. terms of equation (2.6-4) (for the variance calculations; the ground boundary condition changes also in this case). Reformulation of the numerical scheme for non-symmetric plumes is obvious.

Finally, we note that the reader interested in the underlying theoretical fundamentals of the iterative computational scheme of equation (3.3-11) can find relevant information in the monographs of Kubicek and Hlavacek (1982) and Ortega and Rheinboldt (1970).

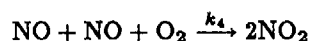
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for Appendix A3.1

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APPENDIX A3.2

**Contribution of Thermal NO Oxidation
to the Formation of NO₂**

In emission inventories nitrogen oxides (NO_x) are often reported as equivalent emissions of nitrogen dioxide (NO₂) even though the exhaust NO_x is composed primarily of nitric oxide (NO). Unless the initial NO₂/NO_x ratio is specified from stack measurements it is necessary to establish appropriate fractions for reconstructing the actual emission levels of NO and NO₂ (McRae et al., 1982). Depending on the source, and the characteristics of the combustion process involved, the above fraction can vary from approximately 1 to 10%. In addition to the NO₂ formed during combustion, some small quantities can be formed in the exhaust gasses by the third order reaction



This reaction step is normally ignored in photochemical reaction mechanisms because of the low ambient levels of nitric oxide. The dependence of $k_4(T)$ on temperature is given by (Baulch et al., 1978)

$$k_4(T) = \frac{1.0666 \times 10^{-5}}{T^2} \exp\left(\frac{530}{T}\right)$$

with T in degrees K. The units of $k_4(T)$ are ppm⁻² min⁻².

McRae et al. (1982) presented a very simple model for the estimation of the fraction of NO which is converted to NO₂ in the vicinity of the source. (Their objective was to develop a simple approach for augmenting the emission inventory of nitrogen oxides). The approach adopted in this simple model is essentially the same with the one described in Appendix A1.1 for the photochemical reaction cycle of nitrogen oxides and ozone. However in the present case plume expansion is determined by the inherent plume dynamics and not by the ambient turbulence.

When the plume is considered to be well mixed across each transverse section in the near field the nitric oxide decay rate is

$$\frac{dc_{NO}}{dt} = -2k_4(T) c_{NO}^2 c_{O_2} + \frac{1}{dt} \frac{D(t)}{dt} (c_{NO} - c_{NO}^b) \quad (\text{A3.2-1})$$

where $D(t)$ is the plume dilution (see Appendix A1.1) and c_{NO}^b is the background concentration of nitric oxide. The nitrogen mass constraint enables the direct calculation of NO₂ from

$$c_{NO_2} = D(t) c_{NO_x}(0) + [1 - D(t)] c_{NO}^b - c_{NO}(t) \quad (\text{A3.2-2})$$

Some comments are useful at this point regarding the NO concentration dynamics downwind from the stack: Entrainment of cool ambient air into the plume causes an increase in the magnitude of $k_4(T)$ (Figure A3.2-1), the plume dilution also results in a reduction of NO. The combined effect of cooling and dilution can be described by integrating the species rate equation. If the background contribution in (A3.2-1) is ignored then the NO concentration decay is given by

$$c_{NO}(t) = \frac{c_{NO}(0) D(t)}{1 + 2c_{NO}(0) \int_0^t k_4(T) \{D(t) c_{O_2} + [1 - D(t)] c_{O_2}^b\} D(t) dt} \quad (A3.2-3)$$

Within the plume, the oxygen and temperature distributions are given by

$$c_{O_2}(t) = c_{O_2}^b + D(t) [c_{O_2}(0) - c_{O_2}^b] \quad (A3.2-4)$$

$$T(t) = T^b + D(t) [T(0) - T^b] \quad (A3.2-5)$$

To describe initial plume dilution McRae et al. used the expression

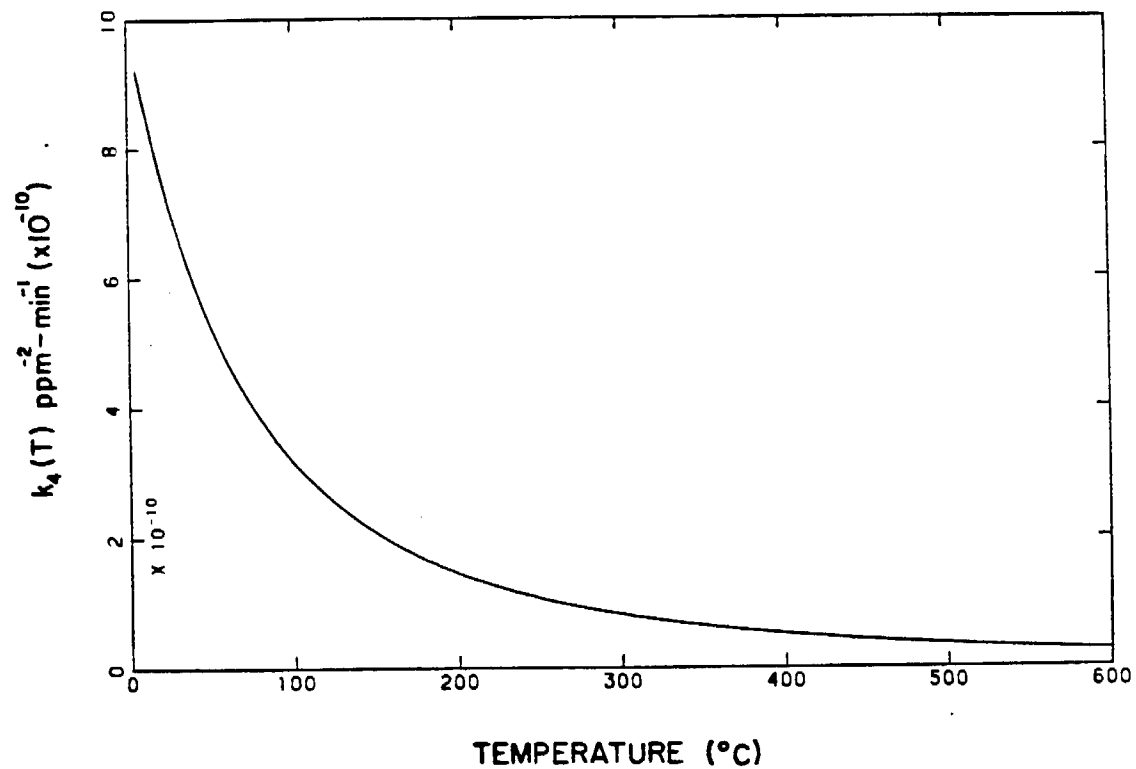
$$D(t) = \exp(-0.15t) \quad (t < 30s) \quad (A3.2-6)$$

Given the initial and background conditions for NO_x , T and O_2 the system of equations (A3.2-1 to A3.2-6) can be solved to give the conversion fractions for short travel times. Figure A3.2-2 (from McRae et al., 1982) presents the results of one such calculation where the initial $NO_2(0)/NO_x$ ratio was 5.0%, $c_{O_2}(0) = 30000$ ppmV, and the instack NO varied from 200 to 2000 ppmV. (A comparison between the pure dilution cases and those in which the chemistry was included indicated that between 2 and 12% of the increase in NO_2 concentration at any travel time can be explained by thermal oxidation.)

This analysis led McRae et al. (1982) to the following conclusions: The first was that, close to the source, thermal oxidation can be significant, which in turn implies that more attention needs to be given to characterizing the stack exhaust gas concentration and temperature distributions when assembling emission inventory information. However since the effects of thermal oxidation are minimal when the dilution is high, there is no need to include this reaction in models dealing with the atmospheric dispersion phase (see Chapter 7) of plume evolution: the incremental conversion can be incorporated by simply increasing the initial NO_2/NO_x emission ratio.

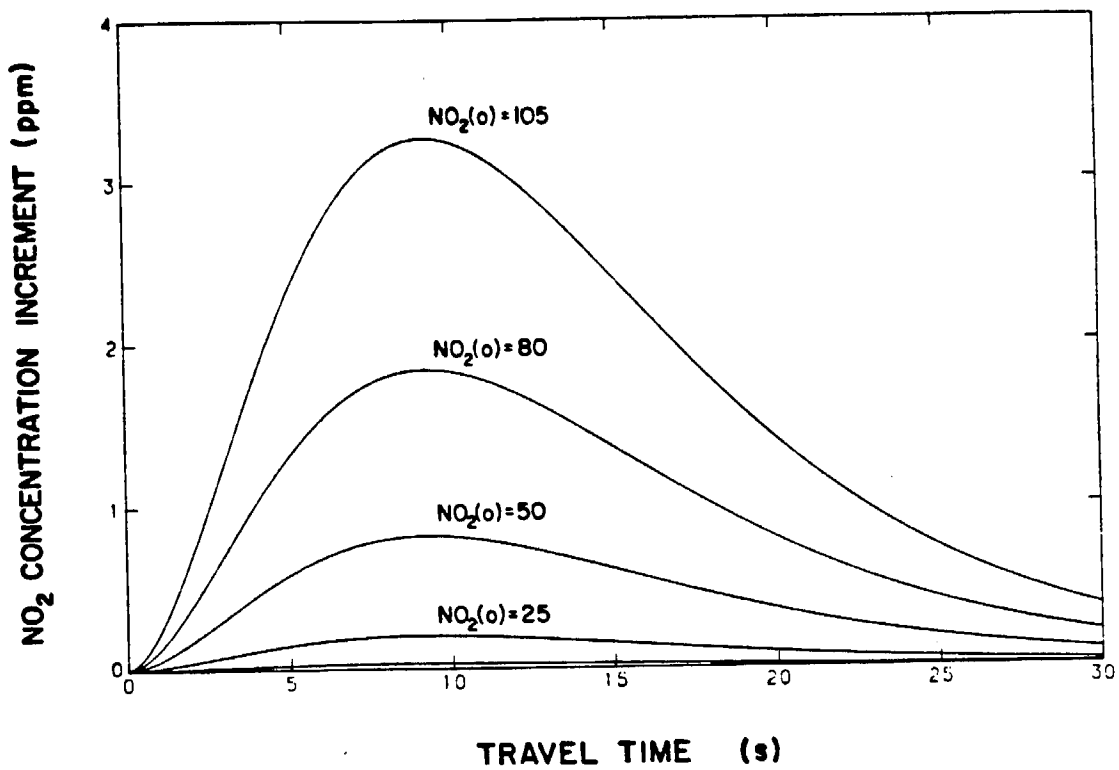
References for Appendix A3.2

- McRae, G.J., Goodin, W.R. and Seinfeld, J.H. (1982) "Mathematical Modeling of Photochemical Air Pollution," Final Report to the State of California Air Resources Board under Contract Nos. A5-046-7 and A7-17-30, EQL Report No. 18, California Institute of Technology, 661 pp.

**Figure A3.2-1**

Variation of the $\text{NO} + \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ Reaction Rate Constant
with Temperature

(Source: McRae et al., 1982)

**Figure A3.2-2**

NO₂ Concentrations as a Function of Travel Time

(Stack Conditions $T = 250^{\circ}\text{C}$, $\text{O}_2 = 3\%$, $\text{NO}_2(0)/\text{NO}_x = 0.05$, $\text{NO}_2^b = 0.02$)

(Source: McRae et al., 1982)

APPENDIX A3.3

The Effect of Temperature Fluctuations

on the Formation of NO_2

(based on Kewley, 1978)

A simplified approach towards assessing the effect of temperature fluctuations on atmospheric reaction rates is to assume that the interaction between the random concentration and temperature fields (the latter being either homogeneous, that is uniform-in-the-mean or, not) takes place only through the dependence of the chemical kinetics on temperature, while all other temperature and flow field interactions are negligible (see also Chapter 4).

In this approach all effects of gradients and turbulent fluctuations of the temperature (or even the radiation) field are incorporated in fluctuating chemical kinetic coefficients. Kewley (1978) employed such a technique to study of the effect of temperature fluctuation on the value of the photostationary state parameter (see Chapter 1) in the atmospheric ozone-nitrogen oxides photolytic cycle. Indeed, if the kinetic coefficients, k_3 , k_1 fluctuate randomly because of their dependence on the temperature which varies randomly inside a plume, one can write

$$k_3 = \langle k_3 \rangle + k'_3$$

$$k_1 = \langle k_1 \rangle + k'_1$$

and thus the relation

$$k_3 c_{\text{NO}} c_{\text{O}_3} = k_1 c_{\text{NO}_2}$$

leads after substitution of Reynolds decomposed quantities, and further ensemble averaging to

$$\begin{aligned} \langle k_3 \rangle \langle c_{\text{NO}} \rangle \langle c_{\text{O}_3} \rangle + \langle k'_3 c'_{\text{NO}} \rangle \langle c_{\text{O}_3} \rangle + \langle k'_3 c_{\text{O}_3} \rangle \langle c_{\text{NO}} \rangle + \langle k_3 \rangle \langle c'_{\text{NO}} c'_{\text{O}_3} \rangle + \langle k'_3 c'_{\text{NO}} c'_{\text{O}_3} \rangle = \\ = \langle k_1 \rangle \langle c_{\text{NO}_2} \rangle + \langle k'_1 c'_{\text{NO}_2} \rangle \end{aligned}$$

Then, the photostationary state parameter defined through

$$\lambda = \frac{\langle k_3 \rangle \langle c_{\text{NO}} \rangle \langle c_{\text{O}_3} \rangle}{\langle k_1 \rangle \langle c_{\text{NO}_2} \rangle}$$

will be given by the relation

$$\lambda = 1 - \frac{1}{\langle k_1 \rangle \langle c_{\text{NO}_2} \rangle} (\langle k'_3 c'_{\text{NO}} \rangle \langle c_{\text{O}_3} \rangle + \langle k'_3 c_{\text{O}_3} \rangle \langle c_{\text{NO}} \rangle + \langle k_3 \rangle \langle c'_{\text{NO}} c'_{\text{O}_3} \rangle + \langle k'_3 c'_{\text{NO}} c'_{\text{O}_3} \rangle - \langle k'_1 c'_{\text{NO}_2} \rangle)$$

Actually Kewley in his calculations assumed k_1 constant because of its less strong dependence on temperature (see Chapter 3). Despite the inherent deficiencies of Kewley's modeling approach regarding the description of dispersion processes (discussed already in Chapter 1), and the further assumption that temperature fluctuations are distributed in exactly an identical manner as concentration fluctuations (a claim for which there is no sufficient experimental support in the case of atmospheric plumes), it is worthwhile to note that these approximate calculations show in general that the effect of the randomness of the temperature field on the overall evolution of the reactive system becomes negligible very soon after the release of the effluents. Typical distances at which λ is estimated to be affected at an observable degree (and for typically strong initial temperature differences) were calculated to be of the order of 100 m downwind the stack and for points close to the plume centerline. It is reasonable therefore to conclude that, under conditions at which temperature variations will not be extremely strong as to induce large density and pressure variations, (and their action is felt only through the dependence of the kinetic coefficients on them), their effect can be neglected, at least at a first approximation, for the $\text{NO}_x\text{-O}_3$ system.

References for Appendix A3.3

- Kewley, D.J. (1978) "Atmospheric Dispersion of a Chemically Reacting Plume," *Atmos. Environ.*, 12, 1895-1900.

PART IB
MATHEMATICAL MODELING
OF TURBULENT REACTING PLUMES

Underlying Concepts